U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-280 756

Source Assessment
Major Barium Chemicals

Monsanto Research Corp, Dayton, Ohio

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio

Mar 78

PB 280 756

United States
Environmental Protection
Agency

Industrial Environmental
Research Laboratory
Cincinnati OH 45268

EPA-600/2-78-004b
March 1978

Research and Development

EPA

Source Assessment: Major Barium Chemicals

Environmental Protection Technology Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-004b	2.
3. RECIPIENT'S ACCESSION NO. PB280756	
4. TITLE AND SUBTITLE: SOURCE ASSESSMENT: MAJOR BARIUM CHEMICALS	5. REPORT DATE: March 1978 issuing date
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): R. B. Reznik and H. D. Toy, Jr.	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Monsanto Research Corporation, 1515 Nicholas Road, Dayton, Ohio 45407	10. PROGRAM ELEMENT NO. 1AB604
	11. CONTRACT/GRANT NO. 68-02-1874
12. SPONSORING AGENCY NAME AND ADDRESS: Industrial Environmental Research Laboratory - Cin., OH, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED: Final
	14. SPONSORING AGENCY CODE: EPA/ 600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report summarizes data on air emissions from the production of major barium chemicals. Compounds studied include barium sulfide, barium carbonate, barium chloride, barium hydroxide, and barium sulfate. In order to evaluate potential environmental effects the source severity, S, was calculated for each emission species from each emission point. Severity is defined as the ratio of the average maximum ground level concentration, $\overline{X}_{max}$, to the ambient air quality standard (for criteria pollutants) or to a reduced TLV (for noncriteria pollutants). The highest values of S occurred for sulfur oxide emissions from the H_2S incinerator (1.89), the black ash rotary kiln (1.51), and the barium hydroxide process exhaust (1.6), and for emissions of soluble barium compounds from product dryers and calciners (0.79 to 200). Various control devices are used to reduce emissions. Scrubbers and baghouses are used on the black ash rotary kiln and on product dryers and calciners. A scrubber and an electrostatic precipitator are employed to control the exhaust from the barium hydroxide process. Byproduct H_2S may be absorbed in caustic instead of being incinerated.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Assessments	Air Pollution Control Source Assessment Source Severity	68A

18. DISTRIBUTION STATEMENT: Release to Public	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 154
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: A08-A01

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE: 1978—260-880/43

EPA-600/2-78-004b
March 1978

SOURCE ASSESSMENT:

MAJOR BARIUM CHEMICALS

by

R. B. Reznik and H. D. Toy, Jr.
Monsanto Research Corporation
Dayton, Ohio 45407

Contract No. 68-02-1874

Project Officer

Mary Stinson
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Edison, N. J. 08817

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains an assessment of air emissions from the production of major barium chemicals. This study was conducted to provide EPA with sufficient information to decide whether additional control technology needs to be developed for this emission source. Further information on this subject may be obtained from the Metals and Inorganic Chemicals Branch, Industrial Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Water Act and solid waste legislation. If control technology is unavailable, inadequate, uneconomical, or socially unacceptable, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

IERL has the responsibility for developing control technology for a large number (>500) of operations in the chemical and related industries. As in any technical program, the first step is to identify the unsolved problems. Each of the industries is to be examined in detail to determine if there is sufficient potential environmental risk to justify the development of control technology by IERL. This report contains the data necessary to make that decision for the production of major barium chemicals.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries

that represent sources of emissions in accordance with EPA's responsibility, as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program, entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer for this series. This study of major barium chemicals was initiated by IERL-Research Triangle Park in August 1974; Mr. Edward J. Wooldridge served as EPA Project Leader. The project was transferred to the Industrial Pollution Control Division, IERL-Cincinnati, in October 1975; Ms. Mary K. Stinson served as EPA Project Officer from that time through completion of the study.

ABSTRACT

This report describes a study of air emissions from the manufacture of major barium chemicals. Compounds studied include barium sulfide, barium carbonate, barium chloride, barium hydroxide, and barium sulfate. Total production of all compounds (except barium sulfide which is primarily an intermediate) is approximately 100,000 metric tons per year.

Emissions released during the manufacturing process consist of particulates, sulfur oxides, nitrogen oxides, carbon monoxide, hydrocarbons, barium compounds, and polynuclear organic materials. Major emission points are the black ash rotary kiln where barite ore is reduced to barium sulfide, the hydrogen sulfide incinerator where byproduct H_2S is burned, the exhaust from the barium hydroxide process, and final product dryers and calciners.

In order to evaluate potential environmental effects the source severity, S, was calculated for each emission from each emission point. Severity is defined as the ratio of the average maximum ground level concentration, $\overline{\chi}_{max}$, to the ambient air quality standard (for criteria pollutants) or to a reduced TLV (for noncriteria pollutants). The highest values of S occurred for sulfur oxide emissions from the H_2S incinerator (1.89), the black ash rotary kiln (1.51), and the barium hydroxide process exhaust (1.6), and for emissions of soluble barium compounds from product dryers and calciners (0.79 to 200).

A variety of control devices is used to reduce emissions. Scrubbers and baghouses are used on the black ash rotary kiln and on product dryers and calciners. A scrubber and an electrostatic precipitator are employed to control the exhaust from the barium hydroxide process. Byproduct H_2S may be absorbed in caustic instead of being incinerated.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This study began in August 1974 and was completed as of August 1977.

CONTENTS

Foreword			iii
Preface			iv
Abstract			vi
Figures			xi
Tables			xii
Abbreviations and Symbols			xiv
Conversion Factors and Metric Prefixes			xvi
I	Introduction		1
II	Summary		2
III	Source Description		10
	A.	Description of the Industry	10
	B.	Process Description	14
		1. Barium Sulfide	16
		2. Barium Carbonate	17
		3. Barium Sulfate	19
		4. Barium Chloride	20
		5. Barium Hydroxide	21
IV	Emissions		23
	A.	Selected Emissions	23
		1. Emissions from Barite Preparation	24
		2. Emissions from the Rotary Kiln	24
		3. Emissions from the H_2S Incinerator	31
		4. $Ba(OH)_2$ Production	32
		5. Emissions from Dryers and Calciners	33
		6. Emissions from Packaging and Shipping	36
		7. Summary	37

Preceding page blank

CONTENTS (Continued)

IV (continued)			
	B.	Emission Characteristics	37
		1. Barite Preparation	37
		2. Rotary Kiln and H_2S Incinerator	39
		3. Dryers and Calciners	40
	C.	Environmental Effects	41
		1. Total Emissions	41
		2. Source Severity	45
		3. Affected Population	52
V	Control Technology		56
	A.	Barite Preparation	56
	B.	Black Ash Rotary Kiln	56
	C.	H_2S Incinerator	59
	D.	Dryers and Calciners	59
	E.	Barium Hydroxide Production	60
VI	Growth and Nature of the Industry		61
	A.	Technology	61
	B.	Industry Production Trends	61
VII	Appendices		64
	A.	Calculation of Production Data	65
	B.	Emissions Calculations	73
	C.	Sampling Program	79
	D.	Polycyclic Organic Materials	97
	E.	Derivation of Source Severity Equations	105
	F.	Derivation of Average Distance From a Source to a Rectangular Plant Boundary	123
	G.	Plume Rise Correlation	130
VIII	Glossary		132
IX	References		134

FIGURES

Number		Page
1	Overall Flow Diagram for Production of Barium Chemicals	3
2	Locations of Plants Producing Barium Chemicals	10
3	Barium Sulfide Production from Barite	16
4	Barium Carbonate from Barium Sulfide and Sodium Carbonate	17
5	Barium Carbonate from Barium Sulfide and Carbon Dioxide/Sodium Carbonate	18
6	Barium Sulfate Production	19
7	Barium Chloride Production	20
8	The Deguide Process for $Ba(OH)_2$ Manufacture	22
9	Variation of $\bar{\chi}$ with Distance	52
10	FMC Double Alkali Scrubber System	58
11	Production Level of Barium Chemicals, 1950-1973	61
A-1	Barite Consumption	66
A-2	Production of BaS and $BaCO_3$	67
A-3	Production of $Ba(OH)_2$ and $BaCl_2$	67
A-4	Production of $BaSO_4$ and BaO	68
A-5	Production of Other Barium Chemicals	68
C-1	Particulate and POM Sampling Train	80
C-2	GCA Sampling Locations	84
C-3	POM Sample Work-up	85
C-4	Mass Spectra for Solution of Standards for Use in POM Analyses	89
F-1	Rectangular Plant Boundary	123
F-2	Coordinate System for Calculating Average Distance	124

TABLES

Number		Page
1	Barium Chemical Producers	2
2	Air Emissions From Barium Chemical Production	5
3	Total Emissions From Barium Chemicals Production	6
4	Source Severity and Affected Population	8
5	List of Barium Chemical Plants	12
6	Estimated 1972 Barium Chemicals Production	13
7	Process Variations and Techniques for Controlling Air Emissions	15
8	Emission Points and Emissions in the Production of Barium Chemicals	23
9	Rotary Kilns Used in the Manufacture of Barium Chemicals	25
10	SO_2 Emissions from Coal/Coke in Rotary Kilns	27
11	SO_2 Emissions from Barite in Rotary Kilns	27
12	POM Emissions from Black Ash Rotary Kiln	30
13	POM Emissions from Coal-Fired Boilers	31
14	Particulate Emissions from a Dryer and Calciner	35
15	Summary of Emission Factors	38
16	Characteristics of Emissions from Rotary Kilns and H_2S Incinerator	40
17	Barium Compounds Dried and Calcined Annually	44
18	Total Emissions from Barium Chemicals Industry	44
19	Total Emissions of Criteria Pollutants by State and Nation	46
20	Emission Severity Equations	48
21	Kiln Stack Heights for Black Ash Rotary Kiln	49

TABLES (Continued)

Number		Page
22	Source Severities for Emissions from Black Ash Rotary Kiln (Without Emission Controls)	50
23	Source Severities for Emissions from Black Ash Rotary Kiln (With Alkaline Scrubber)	50
24	Stack Heights for Dryers and Calciners	51
25	Source Severities for Dryers and Calciners	52
26	Summary of Source Severities and Average Maximum Ground Level Concentrations	53
27	Summary of Affected Population	55
A-1	Estimated Consumption of Barite Raw Material	69
A-2	Production Data for Barium Carbonate	70
A-3	Estimated Production of Barium Carbonate by Manufacturer	71
B-1	Emissions from Gas Fired Burners	74
B-2	Emissions from $BaCO_3$ Dryer and Calciner	74
B-3	Fugitive Dust Emission Rates	76
C-1	Particulate Data	91
C-2	POM Content of Samples	92
C-3	Emission Rates and Emission Factors	93
C-4	Total POM Emissions	96
D-1	Structural Formulas and Carcinogenicity of POM's	98
E-1	Pollutant Severity Equations	105
E-2	Values of a for the Computation of σ_y	107
E-3	Values of the Constants used to Estimate Vertical Dispersion	108
E-4	Summary of National Ambient Air Quality Standards	115
G-1	Plume Rise for Dryers and Calciners	131

ABBREVIATIONS AND SYMBOLS

AAQS	Ambient air quality standard
AMU	Atomic mass unit
A_p	Area of affected population
A, B, C, D, E, F	Atmospheric stability classes
a, b, c, d, e, f	Constants in dispersion equations
a, b; x, y, 1 - x, 1 - y	Sides of a rectangle (a, b) and fractional distances to the sides from a point in the center (Appendix F)
A_R	The ratio $Q/ac\pi u$
B_R	The ratio $-H^2/2c^2$
D	Distance from a ground level source
D_i	Inside stack diameter
D_p	Affected population density
e	Natural logarithm base
F	Hazard factor
H	Effective stack height
h	Physical stack height
ΔH	Plume rise
POM	Polycyclic organic material
P	Total affected population
p	Atmospheric pressure
Q	Mass emission rate
R	Distance from a point in a rectangle to the perimeter
S	Source severity
T_a	Ambient temperature
T_s	Stack gas temperature

ABBREVIATIONS AND SYMBOLS (Continued)

t_0	Instantaneous averaging time of 3 minutes
t	Averaging time
TLV	Threshold Limit Value
u	Wind speed
u, v	Rectangular coordinates (Appendix F)
V_s	Stack gas exit velocity
x, x_1, x_2	Downwind dispersion distances from source of emission release
x_{max}	Downwind distance where maximum ground level concentration occurs
y	Horizontal distance from centerline of dispersion
π	3.14
θ	Polar coordinate angle
σ_y	Standard deviation of horizontal dispersion
σ_z	Standard deviation of vertical dispersion
χ	Downwind ground level concentration at reference coordinate x and y with emission height of H
$\overline{\chi}$	Time average ground level concentration of an emission
χ_{max}	Instantaneous maximum ground level concentration of a pollutant
$\overline{\chi}_{max}$	Time average maximum ground level concentration of a pollutant

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius (°C)	degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
degree Kelvin (°K)	degree Celsius	$t_C^\circ = t_K^\circ - 273.15$
joule (J)	British thermal unit (Btu)	9.479×10^{-4}
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.204
kilogram (kg)	ton (short, 2,000 lb mass)	1.102×10^{-3}
kilometer^2 (km^2)	mile^2	2.591
meter (m)	foot	3.281
meter (m)	mile	6.215×10^{-4}
meter^2 (m^2)	foot^2	1.076×10^{1}
meter^2 (m^2)	inch^2	1.550×10^{3}
meter^3 (m^3)	foot^3	3.531×10^{1}
meter^3 (m^3)	liter	1.000×10^{3}
metric ton	pound	2.205×10^{3}
pascal (Pa)	inch of mercury (60°F)	2.961×10^{-4}
pascal (Pa)	millibars (mb)	1.000×10^{-2}
second (s)	minute	1.667×10^{-2}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
kilo	k	10^3	5 kg = 5 x 10^3 grams
milli	m	10^{-3}	6 mg = 5 x 10^{-3} gram
micro	μ	10^{-6}	5 μm = 5 x 10^{-6} meter
nano	n	10^{-9}	5 ng = 5 x 10^{-9} gram

[a]Metric Practice Guide. American Society for Testing and Materials. Philadelphia. ASTM Designation: E 380-74. November 1974. 34 p.

SECTION I

INTRODUCTION

Air emissions which have a potential effect on the environment are released during the manufacture of barium chemicals. These emissions are characterized in this report as to type, origin, and emission rate. Their potential environmental impact and possible control measures are also discussed.

The following barium compounds, which are made in quantities >4.5 x 10^3 metric tons/yr[a] (5.0 x 10^3 tons/yr), are considered in this study: barium sulfide (BaS), barium carbonate ($BaCO_3$), barium hydroxide [$Ba(OH)_2$], barium sulfate ($BaSO_4$), and barium chloride ($BaCl_2$). Lower volume barium compounds and barite ores which only undergo physical beneficiation are not included.

The barium chemicals industry is dominated by the manufacture of barium carbonate, which is used in glass and ceramics and in the production of barium sulfate and barium hydroxide. Manufacturing begins with barite ore that is reduced in a rotary kiln to barium sulfide. The sulfide serves as an intermediate in the production of other barium compounds.

---

[a] 1 metric ton = 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory pages.

SECTION II

SUMMARY

Barium chemicals constitute a small sector of the inorganic chemicals industry, with total annual production (excluding intermediates) on the order of 1×10^5 metric tons. Over 90% of all production occurs at four plant locations: Chemical Products Corporation in Cartersville, Georgia; FMC Corporation in Modesto, California; Great Western Sugar Company in Johnstown, Colorado; and Sherwin-Williams Company in Coffeyville, Kansas. A list of manufacturers is given in Table 1 along with their representative products.

Table 1. BARIUM CHEMICAL PRODUCERS

Company	Product
Barium and Chemicals, Inc.	(Produces barium chemicals on demand)
Chemical Products Corp.	BaS $BaCO_3$ $BaCl_2$
FMC Corporation	BaS (captive) $BaCO_3$
Great Western Sugar Co.	$BaCO_3$ (captive) $Ba(OH)_2$ (captive)
Mallinckrodt, Inc.	$BaSO_4$
Richardson-Merrell, Inc.	$BaSO_4$
Sherwin-Williams Co.	BaS (captive) $BaCO_3$ $Ba(OH)_2$

Those barium compounds produced in amounts over 4.5×10^3 metric tons/yr (5.0×10^3 tons/yr) include barium sulfide, barium carbonate, barium hydroxide, barium chloride, and barium sulfate. Production (Figure 1) begins with barite ore which is ground, mixed with coal or petroleum coke, and fed into a rotary kiln. In the kiln, $BaSO_4$ is reduced to BaS, commonly known as black ash. The black ash leaves the kiln and passes to a wet ball mill for grinding, after which the soluble BaS is leached out.

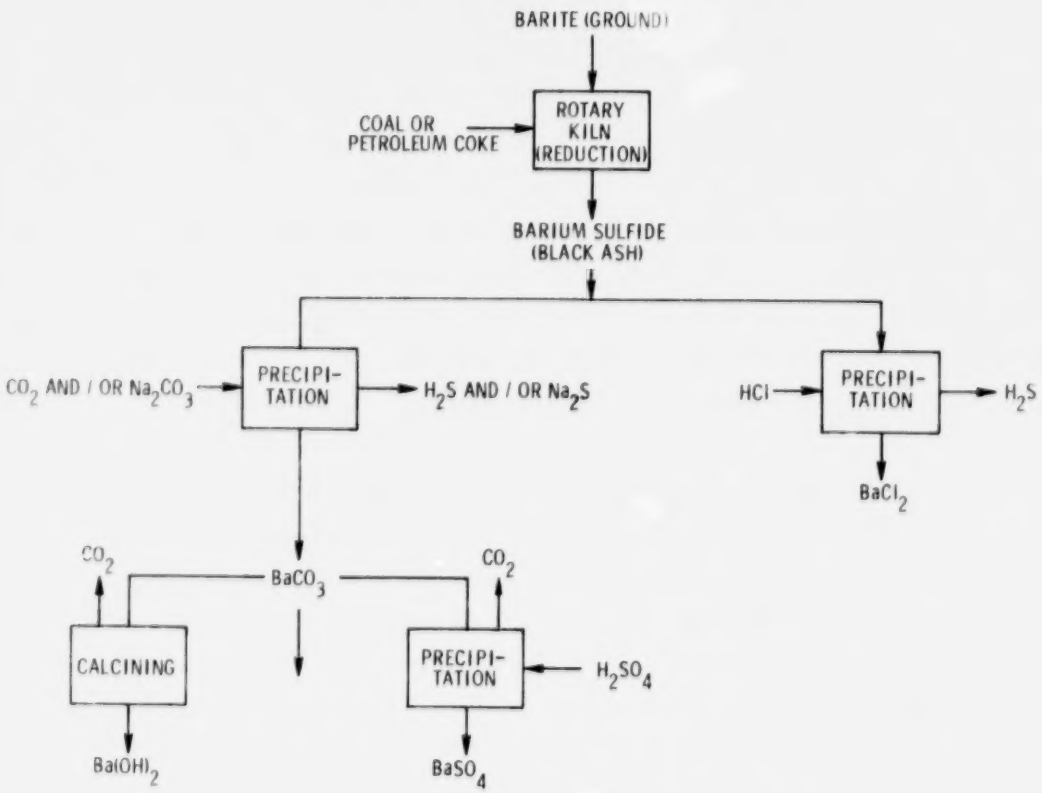


Figure 1. Overall flow diagram for production of barium chemicals

Barium carbonate is produced by reacting BaS solution with CO_2 and/or Na_2CO_3. Barium chloride is prepared by reacting the same solution with HCl. Barium sulfate is manufactured by treating $BaCO_3$ with H_2SO_4. Barium hydroxide is produced by the Great Western Sugar Company from barium carbonate via a barium silicate intermediate. Sherwin-Williams Company employs a different, proprietary process to make its $Ba(OH)_2$.

The estimated 1972 production levels for the various barium compounds are as follows: barite ore (consumption), 9.6×10^4 metric tons (11.6×10^4 tons); BaS, 7.3×10^4 metric tons (8.0×10^4 tons); $BaCO_3$, 4.2×10^4 metric tons (4.6×10^4 tons); $BaCl_2$, 9×10^3 metric tons (9.9×10^4 tons); $Ba(OH)_2$, 12×10^3 metric tons (13.2×10^3 tons); $BaSO_4$, 5×10^3 metric tons (5.5×10^3 tons); and other barium chemicals, $<4.5 \times 10^3$ metric tons ($<5.0 \times 10^3$ tons).

Barium compounds are prepared in solution and must be precipitated or crystallized and then dried before shipment. Barium carbonate for use by the glass industry is also calcined. Where by-product H_2S is formed, it is disposed of either by incineration or by absorption in caustic.

Air emissions generated during barium chemical production consist of the criteria pollutants (particulates, NO_x, SO_x, CO, and hydrocarbons), soluble barium compounds, and polynuclear organic materials (POM's). The emission points are listed in Table 2 together with their associated emissions and emission factors. Where applicable, emission factors are shown for both controlled and uncontrolled conditions. A range of emission factors is provided for dryers and calciners because of their variability of operation.

Table 2. AIR EMISSIONS FROM BARIUM CHEMICAL PRODUCTION

Emission point	Emissions	Emission Factor,[a] g/kg	
		Uncontrolled	Controlled
Barite preparation	Particulate	-[b]	1 ± 75%
Black ash rotary kiln	Particulate	10 ± 50%	≤0.4[c]
	SO_x	25 ± 20%	0.2 to 0.5[d]
	NO_x	0.6 ± 100%	0.6[e]
	CO	5 ± 100%	5[e]
	Hydrocarbons	0.8 ± 100%	0.8[e]
	POM's	0.001 to 0.01	unknown
H_2S Incinerator	SO_x	1,882 ± 1%	-[b]
Barium hydroxide production			
Rotary kiln at Great Western Sugar Co.	Particulate	-[b]	≤0.4[f]
	SO_x	-[b]	0.2 to 0.5[f]
	NO_x	0.6 ± 100%[f]	0.6[e]
	CO	5 ± 100%[f]	5[e]
	Hydrocarbons	0.8 ± 100%[f]	0.8[e]
Sherwin-Williams proprietary process	Particulate	-[b]	<0.5[g]
	SO_x	410 ± 10%	-[b]
	NO_x	0.8 ± 100%	-[b]
	CO	0.11 ± 55%	-[b]
	Hydrocarbons	0.07 ± 140%	-[b]
Barium chemical dryers and calciners	Soluble barium compounds	0.04 to 10	≤0.25

[a] Emission factors for barite preparation, the black ash rotary kiln, and the kiln at Great Western Sugar Co. are per kg of feed material into the kiln. Sulfur oxide emissions from the incinerator are per kg of H_2S burned. The other factors are per kg of final product.

[b] Not applicable.

[c] Based on two kilns equipped with scrubbers.

[d] Based on one kiln with a scrubber.

[e] No data available; assumed to be the same as uncontrolled.

[f] Kiln is equipped with scrubber; emission factor estimated to be the same as for black ash kiln.

[g] Controlled with electrostatic precipitator; emission factor based on control efficiency of electrostatic precipitator units.

Sampling tests were conducted to identify POM emissions from the black ash rotary kiln. Twenty-seven different compounds were identified in the exhaust from a kiln using coal as the reducing agent. Of these, the following are reported to be carcinogenic: methylfluoranthene, benzo(c)phenanthrene, benz(a)anthracene, methyl chrysene, 7,12-dimethylbenz(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, 3-methylcholanthrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, dibenzo(c,g)-carbazole, and dibenzo(a,h and a,i)pyrene. The POM emission rate is similar to that found in coal-fired boilers. It is expected that POM emissions will be less when coke is used as the reducing agent.

Total national emissions from the barium chemicals industry are presented in Table 3. When compared to total national emissions from all stationary sources, they account for less than 0.1% of the national emission burden. Over 95% of the emissions from this industry occur in the states of California, Georgia, Kansas, and Colorado, but the industry contributes less than 1% of the total emissions from these four states.

Table 3. TOTAL EMISSIONS FROM BARIUM CHEMICALS PRODUCTION

Emission	Quantity emitted, metric tons	Percent of national emissions	Percent of combined emissions for California, Colorado, Georgia, and Kansas
Particulates	1,100	<0.01	0.056
SO_x	7,200	0.024	0.72
NO_x	132	<0.01	<0.01
CO	625	<0.01	<0.01
Hydrocarbons	105	<0.01	<0.01

In order to evaluate potential environmental effects, dispersion equations were used to calculate the average maximum ground level concentration, $\bar{\chi}_{max}$, of emissions from the various processing operations (Table 4). For criteria pollutants, $\bar{\chi}_{max}$ was compared to the corresponding ambient air quality standard, AAQS, as a measure of source severity, S:

$$S = \frac{\bar{\chi}_{max}}{AAQS} \qquad (1)$$

For noncriteria emissions, a reduced TLV® was substituted for the AAQS (values for S appear in Table 4):

$$S = \frac{\bar{\chi}_{max}}{TLV \times 8/24 \times 1/100} \qquad (2)$$

The affected population is defined as the number of persons around an emission source who are exposed to an average ground level concentration of an emission greater than the appropriate AAQS or reduced TLV. These values also appear in Table 4 for the various process operations.

Standard control techniques are used in the barium chemicals industry to reduce air emissions. Barite preparation operations are partially enclosed and include spraying with water. One plant has a baghouse on the grinding process. Two of the five black ash rotary kilns in the industry are equipped with alkaline scrubbers and baghouses are being installed on two others.

Emissions of particulates and SO_x during barium hydroxide production are controlled with an alkaline scrubber at Great Western Sugar Company. Particulates are controlled with an electrostatic precipitator at Sherwin-Williams Company.

Table 4. SOURCE SEVERITY AND AFFECTED POPULATION

Emission point	Emission	$\bar{\chi}_{max}$, µg/m³		Source severity		Affected population, persons	
		Uncontrolled	Controlled	Uncontrolled	Controlled	Uncontrolled	Controlled
Barite preparation	Particulates	-[a]	62	-[a]	0.24	-[a]	0
Black ash rotary kiln	Particulates	220	17	0.85	0.066	0	0
	SO_x	550	8.5 to 21	1.51	0.023 to 0.058	35	0
	NO_x	16	32	0.16	0.32	0	0
	CO	190	360	0.0047	0.0091	0	0
	Hydrocarbons	25	48	0.16	0.30	0	0
	POM's	0.022 to 0.22	unknown	0.033 to 0.33	unknown	0	unknown
H_2S Incinerator	SO_x	690	-[a]	1.89	-[a]	67	-[a]
Barium hydroxide	Particulates	-[a]	9.4	-[a]	0.036	-[a]	0
Great Western Sugar Co.	SO_x	-[a]	12	-[a]	0.032	-[a]	0
	NO_x	18	-[a]	0.18	-[a]	0	-[a]
	CO	200	-[a]	<0.01	-[a]	0	-[a]
	Hydrocarbons	27	-[a]	0.17	-[a]	0	-[a]
Sherwin-Williams	Particulates	-[a]	0.69	-[a]	<0.01	-[a]	0
	SO_x	570	-[a]	1.6	-[a]	68	-[a]
	NO_x	1.3	-[a]	0.013	-[a]	0	-[a]
	CO	0.13	-[a]	<0.01	-[a]	0	-[a]
	Hydrocarbons	0.14	-[a]	<0.01	-[a]	0	-[a]
Dryers and calciners	Soluble barium	1.3 to 330	≤9.8	0.79 to 200	≤5.9	0 to 886	18

[a] Not applicable.

The evolution of by-product H_2S during the production of $BaCO_3$ is avoided at one facility by precipitating exclusively with Na_2CO_3. Other producers incinerate H_2S or absorb it in caustic; however, only absorption does not generate additional air pollution in the form of SO_2.

Production levels in the barium chemicals industry are not expected to increase in the future, and may decline. Consequently, air emissions by the industry will remain the same or decrease. The installation of baghouses on the two black ash rotary kilns at one plant will decrease its particulate emissions. Plans are also being made for controlling the one remaining uncontrolled black ash kiln.

SECTION III

SOURCE DESCRIPTION

A. DESCRIPTION OF THE INDUSTRY

The five major barium chemicals [BaS, $BaCO_3$, $BaCl_2$, $BaSO_4$, $Ba(OH)_2$] are manufactured at seven locations in the United States (Figure 2). Major chemicals are defined as those produced in excess of 4.5×10^3 metric tons/yr by a series of chemical reactions. They do not include lower volume barium compounds or barite ores which only undergo physical beneficiation.

Figure 2. Locations of plants producing barium chemicals

The plant sites shown in Figure 2 are so scattered that there is no concentration of the industry. Production is carried on in areas of low population density (<100 persons/km^2, Table 5). The only exception, St. Louis County where Mallinckrodt, Inc., is located, has a population density of 743 persons/km^2. The average population density of the four counties where >90% of all production occurs is 27 persons/km^2.

The companies listed in Table 5 are quite diverse in that they generally produce different types of chemicals and cover a 10-fold range of capacities. Production is dominated by barium carbonate and its precursor, barium sulfide. A brief description of each company is provided below for comparison:

- Chemical Products purchases barite ore and manufactures $BaCO_3$ and $BaCl_2$ via BaS. Barium sulfide is also sold as a final product.[1]
- FMC purchases barite and makes $BaCO_3$ from BaS. They also make $Ba(NO_3)_2$ (<4.0×10^3 metric tons/yr) from $BaCO_3$.[2]
- Sherwin-Williams purchases barite and makes $BaCO_3$ via BaS and $Ba(OH)_2$ by a proprietary process. Another of their products is lithopone (<4.0×10^3 metric tons/yr), a pigment composed of ZnS (28% to 30%) and $BaSO_4$ (70% to 72%) which is made by reacting BaS with $ZnSO_4$.[3]

---

[1]Personal communications. J. L. Gray and R. E. Kotteman, Jr. Chemical Products Corp., Cartersville, Georgia.

[2]Personal communications. R. Brown. FMC Corporation, Modesto, California.

[3]Personal communications. J. J. Nilles and R. W. Hellon. Sherwin-Williams Co., Coffeyville, Kansas.

Table 5. LIST OF BARIUM CHEMICAL PLANTS

Company[a]	Location (city, county, state)	County population density, persons/km^2	Product
Barium and Chemicals, Inc.	Steubenville, Jefferson, Ohio	89	Variety of barium chemicals made on demand
Chemical Products Corp.	Cartersville, Barstow, Georgia	27	BaS $BaCO_3$ $BaCl_2$
FMC Corporation	Modesto, Stanislaus, California	49	BaS $BaCO_3$ $Ba(NO_3)_2$
Great Western Sugar Co.	Johnstown, Weld, Colorado	8	$Ba(OH)_2$ $BaCO_3$
Mallinckrodt, Inc.	St. Louis, St. Louis, Missouri	743	$BaSO_4$
Richardson-Merrell, Inc.	Phillipsburg, Hunterdon, New Jersey	62	$BaSO_4$
Sherwin-Williams Co.	Coffeyville, Montgomery, Kansas	24	BaS $BaCO_3$ $Ba(OH)_2$

[a]Only companies making major barium chemicals are listed. Buckman Laboratories in Memphis, Tennessee, produces barium sulfate from purchased $BaCO_3$ as an intermediate in the production of barium metaborate.

- Great Western Sugar purchases makeup barite and produces $Ba(OH)_2$ from recycled $BaCO_3$. The hydroxide is for captive use in sugar refining and is converted to $BaCO_3$.[4]
- Richardson-Merrell and Mallinckrodt purchase $BaCO_3$ to make $BaSO_4$.[1,3]
- Barium and Chemicals purchases $BaCO_3$ to make other barium chemicals on demand. This company is not considered further in this report since production is on a batch basis.[1]

Production data for barium chemicals are difficult to obtain because government statistics cover only barium carbonate, and individual plants do not disclose such information. The yearly production level is also dependent on the economy. Estimated 1972 production is calculated in Appendix A and summarized in Table 6. Over 90% of all production occurs at Chemical Products Corp., FMC Corp., Great Western Sugar Co., and Sherwin-Williams Co.

Table 6. ESTIMATED 1972 BARIUM CHEMICALS PRODUCTION

Compound	1972 Production, 10^3 metric tons
Barite ore (consumption)	96
BaS (intermediate)	73
$BaCO_3$	42
$BaCl_2$	9
$Ba(OH)_2$	12
$BaSO_4$	5
Other barium compounds	<4.5

[4]Personal communications. D. Muller. Great Western Sugar Co., Johnstown, Colorado.

The barium chemicals industry employs many process variations and control techniques which influence the types and amounts of air emissions released during production. The important ones are listed in Table 7.[1-4] As a result, there is no representative plant or process in the industry.

B. PROCESS DESCRIPTION

The starting point in the manufacture of barium chemicals is barite (baryte) ore, which is primarily barium sulfate. Barite is mined in seven states (Alaska, Arkansas, California, Georgia, Missouri, Nevada, Tennessee) and serves not only as the raw material for barium chemicals but also as an ingredient in oil well drilling muds.[5] The average analysis of chemical grade barite is $BaSO_4$, 94% to 96%; Fe_2O_3, 0.8% to 2.0%; $SrSO_4$, 0.1% to 2.0%; $BaCO_3$, 1%; SiO_2, 3.0% to 6.0%; H_2O, 0.5% to 2.0%; F, Pb, and Zn, nil.[6] Before shipment to consumers, the ore is washed with hot water to remove impurities. It is then crushed and agitated with water in a jig for further purification. The barite may then be shipped or it may be further processed by milling and magnetic separation.

After it arrives at a plant site, the partially purified barite is milled (if necessary), mixed with coal or petroleum coke, and reduced in a rotary kiln to barium sulfide, which is an intermediate in the production of barium chloride and barium carbonate. A flow diagram of the overall process was shown earlier in Figure 1.

---

[5]Fulkerson, F. B. Barite. In: Minerals Yearbook 1972, Volume I: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1974. p. 181-187.

[6]Preisman, L. Barium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition. Vol. 3, Standen, A. (ed.). New York, Interscience Publishers, Division of John Wiley & Sons, Inc., 1964. p. 80-99.

Table 7. PROCESS VARIATIONS AND TECHNIQUES FOR CONTROLLING AIR EMISSIONS[1-4]

Process	Variation/control technique	Emissions affected
Barite ore preparation	Ore may be milled before or after it arrives at plant site	Fugitive dust
	Water spray at grinding operation	Fugitive dust
	Operations partially enclosed; exhausted through baghouse	Fugitive dust
Rotary kiln to reduce barite to BaS	Coal or petroleum coke may be used as a reducing agent	POM; hydrocarbons
	Different types of ore and degree of milling	Particulate
	Variable sulfur content of coal/coke	SO_x
	Add-on scrubber	Particulate; SO_x
Barium carbonate production	Precipitation with Na_2CO_3 or CO_2; latter generates H_2S which must be absorbed or incinerated	SO_x
Barium hydroxide production	Two completely different processes with different controls	Particulate; SO_x; NO_x; CO; hydrocarbons
Product dryers and calciners	At least five different types of dryers and calciners are used	Soluble barium compounds
	Add-on baghouse	Soluble barium compounds
	Add-on scrubber	Soluble barium compounds

1. Barium Sulfide

Barium sulfide or black ash is made by reducing barite ($BaSO_4$) in a rotary kiln with coal or petroleum coke (Figure 3). Unmilled barite ore is first ground, then mixed with coal or coke in a ratio of 3 to 4 parts barite per 1 part coal or coke. One of the black ash manufacturers uses coal as a reducing agent while the others use petroleum coke.[1-4] The mixture is fed into a rotary kiln where the temperature is raised to between 900°C and 1,200°C by gas heating.

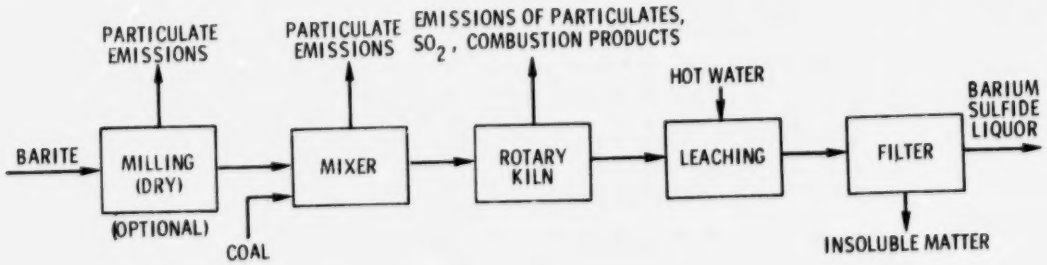


Figure 3. Barium sulfide production from barite

Inside the kiln barium sulfate is reduced by carbon to barium sulfide. The reaction shown below is thought to occur:

$$BaSO_4 + 4C \rightarrow BaS + 4CO \qquad (3)$$

since a blue flame typical of CO combustion can be observed above the bed of materials in the kiln.[1]

The conversion reaction is approximately 90% efficient (the general range is 85% to 95%). The variation in percent BaS formed is due to the presence of iron and silica impurities which cause side reactions producing complex water-insoluble,

but acid-soluble, barium silicate, ferrate, and carbonate. The water-soluble barium sulfide is leached from the black ash with hot water and filtered to remove any remaining insoluble matter. The resulting solution, containing 17% to 18% BaS, is then ready to feed into the barium carbonate or barium chloride process.[6]

Exhaust gases from the rotary kiln pass through cyclones before going to the atmosphere. Stack emissions include particulates, SO_x, NO_x, CO, hydrocarbons, and POM's (polynuclear organic materials). The remaining process emissions are fugitive dust emissions from grinding (milling) and mixing.

2. Barium Carbonate

Barium carbonate is manufactured from barium sulfide by two precipitation processes: precipitation with Na_2CO_3, or precipitation with CO_2 followed by precipitation with Na_2CO_3. In the first process the following reaction occurs:

$$BaS_{(aq)} + Na_2CO_3(aq) \xrightarrow{60\text{-}70°C} BaCO_3 \downarrow + Na_2S_{(aq)} \quad (4)$$

The resulting slurry is washed, filtered, and dried (Figure 4). The dried barium carbonate is then ground to the desired size and packaged. This process is used by about 50% of the industry; actual production data are unavailable.[1-4]

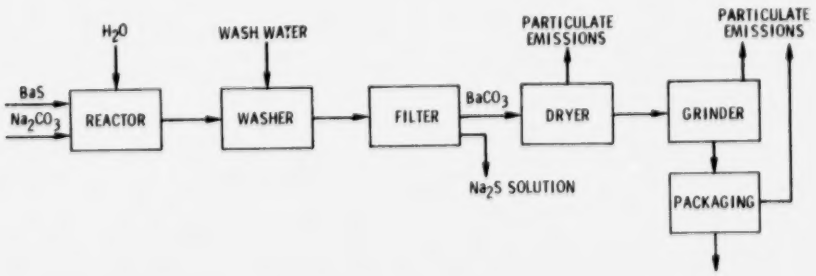


Figure 4. Barium carbonate from barium sulfide and sodium carbonate

In the second process (Figure 5), carbon dioxide, obtained from the stack gas of the rotary kiln, is bubbled through a barium sulfide solution and causes the following reaction:

$$BaS_{(aq)} + CO_2(g) + H_2O \xrightarrow{40\text{-}90°C} BaCO_3 \downarrow + H_2S_{(g)} \quad (5)$$

This reaction removes 95% of the BaS in a series of concentration steps. In the repulper, Na_2CO_3 is added and reacts with the remaining BaS as shown in Equation 4. The product is thickened, filtered, and dried at 50°C to 100°C.[1,3] Barium carbonate for use in the glass industry (about 30% of production) is further processed in a calciner (at 400°C to 450°C). This produces a densified product which can be mixed with other glass raw materials without segregation.[1,3]

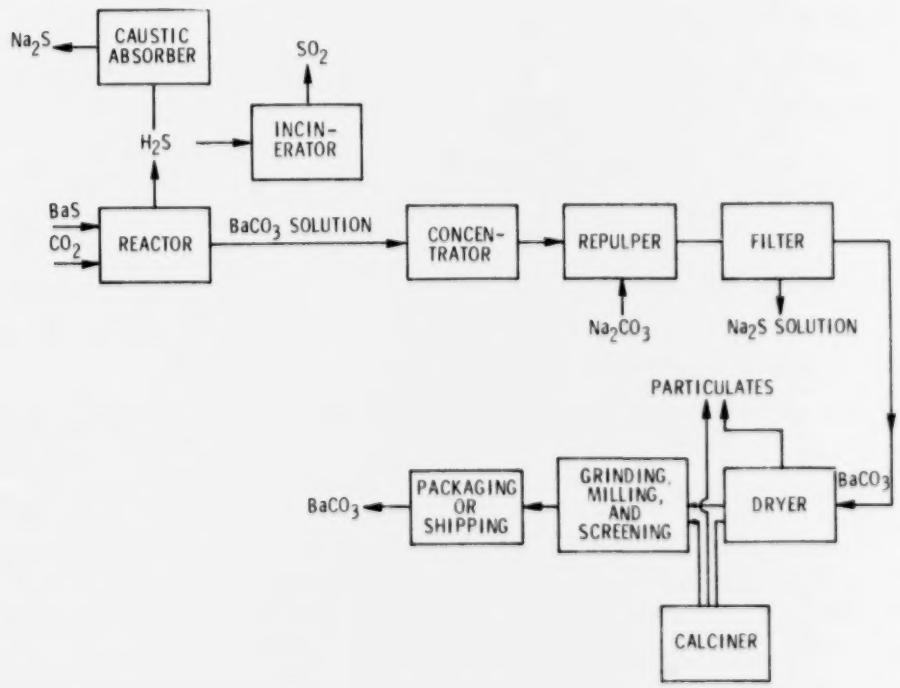


Figure 5. Barium carbonate from barium sulfide and carbon dioxide/sodium carbonate

By-product H_2S is either absorbed in caustic to produce Na_2S or incinerated to give SO_2. One company uses incineration while another practices both techniques. Two carbonate producers do not generate H_2S.[1-4]

The dry barium carbonate is ground and screened to the desired size range, then packaged for shipment. Large volumes are bulk shipped in railroad hopper cars.

Particulate emissions in the production of barium carbonate arise from drying, calcining, grinding, screening, and packaging. Combustion products are emitted from the dryers and calciner. If H_2S is incinerated, SO_2 is also released.

3. Barium Sulfate

Synthetic barium sulfate is produced by the reaction of $BaCO_3$ with H_2SO_4 (Figure 6).[1] The reaction is:

$$BaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow BaSO_4\downarrow + H_2O + CO_{2(g)} \quad (6)$$

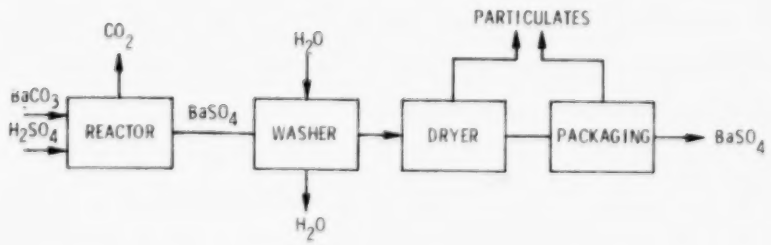


Figure 6. Barium sulfate production

The product is washed, dried, and packaged. The last two steps are sources of particulate emissions.

4. Barium Chloride

Barium chloride is manufactured by reacting barium sulfide solution with hydrochloric acid (Figure 7) as follows:

$$BaS_{(aq)} + 2HCl_{(aq)} \rightarrow BaCl_2 \downarrow + H_2S_{(g)} \qquad (7)$$

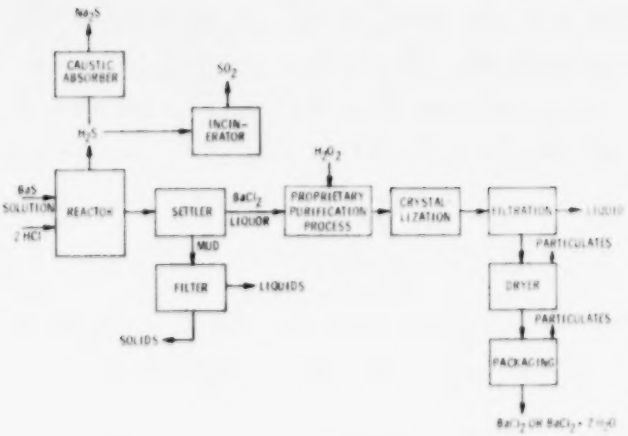


Figure 7. Barium chloride production[1]

A rubber-lined, agitated reaction vessel is used with a gas outlet pipe. Standard hydrochloric acid (20° Be, 31.45% HCl) is used to form the barium chloride.[1,6] The resulting solution is filtered of solids and then purified by a proprietary process. The barium chloride liquor is concentrated, then evaporated and crystallized in the same step. The crystals are dewatered in a pan filter and dried. Barium chloride is packaged in moisture-proof steel or fiber drums.

By-product H_2S is either absorbed in a caustic solution or incinerated to SO_2. The exact amount incinerated is unknown, but the manufacturer indicated that H_2S is generally absorbed

in caustic. In addition to SO_2, the manufacturing process causes emissions of particulates from drying and packaging.

5. Barium Hydroxide

Barium hydroxide is manufactured by two companies using different processes. The Sherwin-Williams Co. uses a proprietary process to make the monohydrate. Emissions of particulates, SO_2, and combustion products (gas heating) are given off in their process. Particulates from the operation are controlled by an electrostatic precipitator.[3] The product dryer also causes particulate emissions.

The Great Western Sugar Co. uses the Deguide process to make barium hydroxide for use in sugar purification. It is based on the reaction between barium carbonate and monobarium silicate to form tribarium silicate:[7]

$$2BaCO_3 + BaSiO_3 \rightarrow Ba_3SiO_5 + 2CO_2 \qquad (8)$$

The silicate is hydrolyzed to form barium hydroxide and monobarium silicate which is recycled:

$$Ba_3SiO_5 + 2H_2O \rightarrow 2Ba(OH)_2 + BaSiO_3 \qquad (9)$$

The hydroxide is used in sugar purification and is finally converted to $BaCO_3$ which is also recycled.[7] Recycle of the barium compounds is the key to the economic success of this

---

[7]Dahlberg, H. W., and R. J. Brown; revised by W. Newton, II, and M. G. Auth. The Barium Saccharate Process. In: Beet-Sugar Technology, Second Edition, McGinnis, R. A. (ed.). Fort Collins, Colorado, Beet Sugar Development Foundation, 1970. p. 573-578.

process. A flow diagram of the overall process appears in Figure 8.

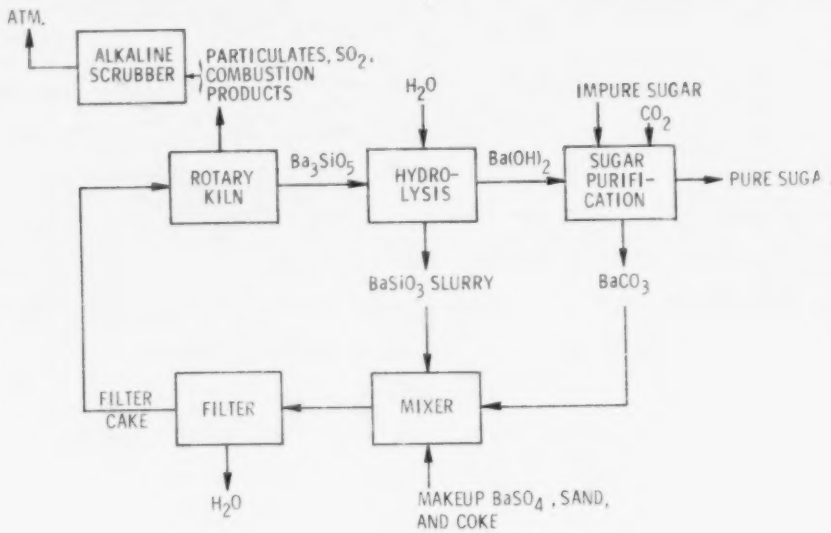


Figure 8. The Deguide process for $Ba(OH)_2$ manufacture[7]

Barium sulfide and H_2S are not formed as products in the Deguide process although they may exist as reaction intermediates in the kiln. Instead, makeup barite, sand, and coke are added to the recycled $BaSiO_3$ and $BaCO_3$ before the mixture is fed into the rotary kiln. The overall reaction that occurs is then:

$$6BaSO_4 + 2SiO_2 + 3C + \rightarrow 2Ba_3SiO_5 + 6SO_2 + 3CO_2 \quad (10)$$

No information is available on the amount of makeup $BaSO_4$ that is added.

Exhaust gases from the rotary kiln are controlled by an alkaline scrubber.[4] The only other air emission is fugitive dust from the preparation and handling of makeup barite, sand, and coke.

SECTION IV

EMISSIONS

A. SELECTED EMISSIONS

The various emission points in the production of barium chemicals are listed in Table 8 along with their respective emissions. Combustion products from dryers and calciners were not studied in detail because calculations (Appendix B) showed them to be negligible (<100 metric tons/yr for the entire industry).

Table 8. EMISSION POINTS AND EMISSIONS IN THE PRODUCTION OF BARIUM CHEMICALS

Process or operation	Emission
Grinding and milling of barite; mixing with coal or coke	Particulates (fugitive)
Barium sulfide rotary kiln	Particulates, SO_x, NO_x, CO, hydrocarbons, POM's (stack)
H_2S incinerator	SO_2 (stack)
Barium hydroxide production	Particulates, SO_x, NO_x, CO, hydrocarbons (stack)
Product dryers and calciners	Particulates, combustion products (stack)
Packaging and shipping	Particulates (fugitive)

1. Emissions from Barite Preparation

Barite ore must be ground and mixed with coal or coke before it is fed into the rotary kiln. This processing is a source of fugitive dust emissions whose magnitude depends on the extent to which the operations are enclosed. Water sprays are also employed to control emissions. (At one site, the ore is milled before it arrives at the plant.) No data could be found in the literature on emissions from barite preparation nor have they been measured by any of the manufacturing companies.

One of the four major barium chemical plants was sampled in order to assess the severity of fugitive dust emissions from barite preparation. The sampling procedure and analytical results are given in Appendix C. The emission factor was found to be 1 g/kg ± 75% (Appendix B.2).

2. Emissions from the Rotary Kiln

Rotary kilns are used in the manufacture of barium chemicals at the four plants shown in Table 9. The kilns are exhausted through cyclones to reduce process loss (∿5% loss without cyclones; ∿0.5% loss with cyclones).[1] Table 9 identifies the additional control devices on the kilns.

The rotary kiln at Great Western Sugar produces tribarium silicate instead of barium sulfide (Section III.B.5). Consequently, the emission factors developed in this section of the report cannot be directly applied to that kiln. Although emissions data are not available on the kiln, state emission standards for SO_x and particulates are met using an alkaline scrubber.

Table 9. ROTARY KILNS USED IN THE MANUFACTURE OF BARIUM CHEMICALS[1-4]

Company	Product from kiln	Number of kilns	Controls (after cyclones)
Chemical Products	BaS	2	Baghouses are being installed
FMC	BaS	1	Double alkali scrubber
Sherwin-Williams	BaS	2	None on large kiln; scrubber on small kiln
Great Western	Ba_3SiO_5	1	Alkaline scrubber

a. Particulates - Particulate emissions in rotary kilns are caused by the entrainment of dust particles in the feed material. Emission level is a function of the type of barite ore used, how finely it is ground, and the air flow rate through the kiln. All kilns are equipped with cyclones which reduce process loss from ∿5% to ∿0.5%. Additional control measures are employed at some plants (Table 9).

Uncontrolled dust emissions from the kiln range from 5 to 15 g/kg of feed material because of the variations in operation mentioned above.[1-3]

Sampling measurements taken on one kiln during the course of this study (Appendix C) yielded an emission factor of 6.25 g/kg ± 15% of feed material. An average value of 10 g/kg ± 50% is used in this report.

One company reported data on a kiln equipped with a scrubber. Emissions varied from 150 g/hr to 180 g/hr while the ore feed rate ranged from 29 kg/min to 33 kg/min. The equivalent emission factor is 0.07 g/kg ± 14% of feed material, which corresponds to approximately 99% efficiency.

Another scrubber had an emission factor of 0.4 g/kg, equivalent to a 96% efficiency. This scrubber was designed for SO_x rather than particulate removal.

b. $\underline{SO_x}$ - Sulfur oxides are produced in the rotary kiln by the oxidation of sulfur present in the coal or petroleum coke used as a reducing agent, and by side reactions in which $BaSO_4$ reacts with impurities in the ore to give insoluble barium compounds and SO_x. Hence, SO_x emissions depend on the sulfur content of the coal/coke and the level of impurities in the ore.[1,2] These parameters vary from producer to producer, as well as from one time period to another for the same producer.

One manufacturer reported average SO_x emissions of 22.4 g/kg of feed material, with maximum emissions of 25.6 g/kg. Another producer had an average uncontrolled emission factor of 27.5 g/kg. The second producer was using a higher silica ore, although neither company disclosed its exact ore composition.

In order to verify the SO_x emission factors, material balance calculations were performed for the two SO_x formation mechanisms described above as summarized below:

- For coal/coke having a sulfur content of 1% to 7%, SO_2 emission factors appear in Table 10. These are based on the stoichiometric conversion of sulfur to sulfur dioxide, and a feed ratio of 4 parts barite to 1 part coal/coke.

Table 10. SO_2 EMISSIONS FROM COAL/COKE IN ROTARY KILNS

Sulfur content of coal/coke, %	SO_2 emission factor, g/kg of feed material
1	4
2	8
3	12
4	16
5	20
6	24
7	28

For barite ore composed of 95% $BaSO_4$, with a conversion ratio to BaS of 90% to 95%, the SO_2 emission factors are given in Table 11. The feed material is 4 parts barite to 1 part coal/coke, and all of the $BaSO_4$ lost is assumed to yield SO_2.

Table 11. SO_2 EMISSIONS FROM BARITE IN ROTARY KILNS

Conversion of $BaSO_4$ to BaS, %	SO_2 emission factor, g/kg of feed material
90	21
91	19
92	16.5
93	14.5
94	12.5
95	10.5

Tables 10 and 11 agree with the reported SO_x emission factors. The combined emissions are higher than expected, but the assumed stoichiometric conversion is a worst case situation. An average uncontrolled emission factor for SO_x of 25 g/kg ± 20% of feed material is used in this report.

One company, which had installed a scrubber system specifically to control SO_x emissions, reduced them to 0.2 g/kg to 0.5 g/kg, corresponding to a control efficiency of 98% to 99%. The system has reduced the stack gas concentration of SO_x from 5,000 ppm to as low as 52 ppm.

c. NO_x - No measurements have been made for NO_x emissions, which result from the combination of atmospheric nitrogen and oxygen in the combustion zone of the kiln. An emission factor was estimated based on the rate of fuel consumption, which was reported to be 150 m^3/metric ton of BaS produced.[3] The emission factor is 0.6 g/kg ± 100% of feed material (Appendix B.3).

d. CO and Hydrocarbons - No data have been reported for emissions of carbon monoxide and hydrocarbons from the rotary kiln. One company stated that none were detected in the stack gases by an Orsat analysis, which has a detection limit on the order of 0.1%, or 1,000 ppm. However, since coal is used as a reducing agent, these emissions were expected to be present. Therefore, a sampling test was performed for CO and hydrocarbons as described in Appendix C. The emission factor for CO is 5 g/kg ± 100%, and that for hydrocarbons is 0.1 g/kg ± 100% (Appendix B.4).

e. POM's - Polynuclear organic materials (POM's) are known to be emitted from combustion processes. Their formation is favored under poor combustion conditions (insufficient oxygen) and when coal or wood is used as a fuel instead of gas or oil. POM's are of importance because some of them are known to be carcinogenic [e.g., benzo(a)pyrene][8] (Appendix D).

---

[8]Particulate Polycyclic Organic Matter. Washington, National Academy of Sciences, 1972. 361 p.

Although no measurements had been made for POM's from the black ash kiln, their presence was assumed since coal/coke was used as a reducing agent. Consequently, sampling tests were conducted to determine the level of POM emissions from the rotary kiln (Appendix C). The results given in Table 12 indicate that 27 compounds were detected, of which 14 have shown carcinogenic activity in animals.

The kiln that was tested used coal as a reducing agent. It is believed that petroleum coke would yield lower POM emissions since coke is prepared by heating petroleum to drive off all volatile compounds. For confirmation, a petroleum coke sample was extracted with pentane and the extract analyzed by gas chromatograph-mass spectrometry. No POM's were detected.

To compare the magnitude of POM emissions, Table 13 lists the results of a series of tests on coal-fired boilers.[9] Emission factors for each compound are given in µg/kg of fuel burned. The data show that rotary kiln emissions are in the same range as those from coal-fired boilers.

In subsequent calculations, a range of 0.01 g/kg to 0.001 g/kg of feed material is used for the POM emission factor. Kilns equipped with scrubbers or using coke as a reducing agent are expected to exhibit lower emissions.

---

[9]Hangebrauck, R. P., D. J. Von Lehmden, and J. E. Meeker. Emissions of Polynuclear Hydrocarbons and other Pollutants from Heat-Generation and Incinerator Processes. Journal of the Air Pollution Control Association. 14:267-278, July 1964.

TABLE 12. POM EMISSIONS FROM BLACK ASH ROTARY KILN

Compound	Hazardous rating[a]	Emission factor, µg/kg
Dibenzothiophene	-	520 to 2,400
Anthracene	-	320 to 4,500[b]
Phenanthrene	-	
Methylanthracenes[c]	None[d]	100 to 670[b]
Methylphenanthrenes[c]	None[e]	
Fluoranthene	-	45 to 470
Pyrene	-	20 to 210
Methylpyrenes[c]	-	19 to 70[b]
Methylfluoranthenes[c]	None[f]	
Benzo(c)phenanthrene	+++	0 to unknown[h] 42
Naphthobenzothiophene[g]	-	
Chrysene	±	120 to 590[b]
Benz(a)anthracene	+	
Methylchrysenes[c]	±	29 to 110
7,12-Dimethylbenz(a)anthracene	++++	0 to 13
Benzo(b)fluoranthene[i]	++	82 to 435[b]
Benzo(k)fluoranthene	-	
Benzo(a)pyrene	+++	30 to 83[b]
Benzo(e)pyrene	-	
Perylene	-	
3-Methylcholanthrene	++++	0 to 36
Indeno(1,2,3-cd)pyrene	+	0 to 61
Benzo(g,h,i)perylene	-	0 to 13
Dibenz(a,h)anthracene	+++	0 to 63
7H-Dibenzo(c,g)carbazole	+++	0 to 23
Dibenzo(a,i)pyrene[j]	+++	0 to 45[b]
Dibenzo(a,h)pyrene[k]	+++	
Total POM's		1,100 to 8,700

[a] Hazardous rating scale is:[9]
- not carcinogenic
± uncertain or weakly carcinogenic
+ carcinogenic
++, +++, ++++ strongly carcinogenic

[b] These compounds were not resolved on the gas chromatograph - mass spectrometer.

[c] The different methyl isomers were not resolved on the gas chromatograph - mass spectrometer.

[d] No rating given in Reference 8; 9-methyl isomer is listed as a neoplastic agent in the 1974 Toxic Substances List.[10]

[e] No rating given in Reference 8.

[f] No rating given in Reference 8; 2-methyl isomer is listed as a carcinogenic agent and 3-methyl isomer as a neoplastic agent in the 1974 Toxic Substances List.[10]

[g] Indexed in Chemical Abstracts as benzonaphthothiophenes of which there are three, namely, benzo(b)naphtho(1,2-d 2, 1-d 2,3-d)thiophene; these isomers could not be resolved with the analytical method used.

[h] The mass ion for this compound was detected but no standard was available.

[i] Indexed in Chemical Abstracts as benz(e)acephenanthrylene.

[j] Indexed in Chemical Abstracts as benzo(rst)pentaphene.

[k] Indexed in Chemical Abstracts as dibenzo(b,def)chrysene.

- - - - - - - - - - -

[10] The Toxic Substances list 1974 Edition, Christensen, H.E., and T. T. Luginbyhl (ed.). Rockville, Maryland, U.S. Department of Health, Education and Welfare, June 1974. 904 p.

Table 13. POM EMISSIONS FROM COAL-FIRED BOILERS[9]
(μg/kg fuel)

Compound	Test unit						
	1	2	3	4	5	6	7
Anthracene		11			26		
Phenanthrene					309	29	875
Fluoranthene	4.6	16	18	10	1,170	95	1,420
Pyrene	3.8	7.1	10	17	494	51	231
Benz(a)anthracene	0.49				120		17
Benzo(a)pyrene	0.49	0.95	0.97	0.77	309	3.5	115
Benzo(e)pyrene		2.7	3.3	10	245	6.9	163
Perylene					48		
Benzo(g,h,i,)perylene					139		17
Anthanthrene					9.0		
Coronene				0.77	10		35

Note: Blanks indicate no POM emissions detected.

3. Emissions from the H_2S Incinerators

Only two companies operate H_2S incinerators. Another plant precipitates barium carbonate with Na_2CO_3, while Great Western Sugar does not make $BaCO_3$ via BaS.[1-4] No sampling measurements were performed on the incinerators. Instead, the emission factor for SO_2 was calculated from a material balance, based on the reaction:

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \qquad (11)$$

The emission factor is 1.882 kg SO_2 per kg of H_2S burned. The accuracy is estimated to be within 1% since the oxidation reaction proceeds to completion.

4. $Ba(OH)_2$ Production

Stack emissions from the production of barium hydroxide are difficult to assess since two different processes are used, one of which is proprietary. At Great Western Sugar, a rotary kiln is used to make tribarium silicate from recycled monobarium silicate and barium carbonate. There are no other sources of stack emissions since the barium compounds are not dried.[4] (Fugitive emissions for all barium chemicals are discussed in Section IV.A.1.)

Emissions from the rotary kiln consist of particulates, SO_x from makeup barite ore and coke, and combustion products, NO_x, CO, and hydrocarbons. An alkaline scrubber is used to control particulates and SO_x emissions in order to meet state standards. It is believed that the emission factors developed for the black ash rotary kiln would apply to this kiln also, as a first approximation, because the kiln design is the same.

The amount of sulfur oxide emissions should be the same because of two opposing factors. The sulfur in the feed material should be less because only makeup barite and coke are used, but the SO_x released should be greater since no BaS is made. All of the $BaSO_4$ is converted to tribarium silicate and SO_2. Therefore, SO_x emissions are estimated to be comparable to those from the BaS rotary kiln.

Information on the Sherwin-Williams process for manufacturing $Ba(OH)_2$ is proprietary. Emissions from raw material preparation and product drying are considered in Sections IV.A.1 and IV.A.5, respectively. Emissions from the rest of the process are exhausted through stacks equipped with electrostatic precipitators for particulate control.[3] No data are available, but particulate emissions are judged to be <0.5 g/kg.

Emissions of SO_2 were reported to be equimolar to $Ba(OH)_2$ production, plus a small additional quantity for process loss (estimated at ∿10%).[3] The emission factor is then 410 g SO_2/kg of $Ba(OH)_2$ produced (±10%).

Emissions of combustion products were estimated based on reported fuel usage rate and the emission factors derived in Appendix B.1. Fuel used for drying was estimated and subtracted from total fuel burned. The following emission factors were calculated: NO_x, 0.8 g/kg; CO, 0.11 g/kg; and hydrocarbons, 0.07 g/kg.

5. Emissions from Dryers and Calciners

Particulate emissions from dryers and calciners are important because $BaCO_3$, $BaCl_2$, and $Ba(OH)_2$ are considered to be hazardous compounds (Section IV.B). Barium sulfate is inert and nonhazardous.

Various types of dryers are used in the industry. Those in use at the major companies are listed below:[1-3]

Type of dryer	Number in use
Rotary	4 (one is a predryer)
Drum	1
Flash	1
Spray	1

Calciners (three) are all of the rotary design (i.e., an inclined cylinder which rotates on its axis). Dryers and calciners are heated with gas and have a dust trap before the exhaust stack. In addition, three of the dryers and one of the three calciners are equipped with baghouses to further control particulate emissions. Another dryer is controlled with a wet scrubber.[1-3]

The parameters that determine the amount of uncontrolled particulates emitted by dryers and calciners include the specific equipment design, the size of particles being processed, the moisture content of the final product, and the air flow rate through the kiln. Variations in these parameters may change the emission factor more than 200-fold (from ~0.04 g/kg to 10 g/kg). Plume opacities may vary from 0% to 30%.[1-3]

Because the industry is small and diversified, there is no representative dryer. Moreover, emissions data are too limited to establish a quantitative relationship between dryer parameters and emission factors. The following qualitative comments can be made.

- Finer sized particles produce dust more readily. As an example, $BaCl_2$ crystals are larger than those of $BaCO_3$, and calcined $BaCO_3$ is of a larger grain size than uncalcined material. Other things being equal, $BaCl_2$ will dust less than $BaCO_3$, and calcined $BaCO_3$ less than uncalcined $BaCO_3$.
- A higher moisture content in the final product will reduce emissions. As an example, barium chloride is often prepared as the dihydrate, and stack opacity is near 0%.[1]
- A higher air flow rate through the kiln causes increased dusting. This occurs, for instance, when the production rate is increased.

Only limited testing has been performed on dryers and calciners. Test data for one rotary dryer and one calciner are presented in Table 14. Measurements were not performed according to EPA Method 5, and the results are of unknown accuracy.

Table 14. PARTICULATE EMISSIONS FROM A DRYER AND CALCINER

Parameter		Rotary dryer	Rotary calciner
Emission, mg/sec	Run 1	7.49	27.22
	Run 2	36.82	
	Run 3	26.95	40.73
	Average	23.75	33.98
Allowable emission, mg/sec		955.8	678.4
Process flow rate, metric tons/hr (taken from state regulations for emission standards)		2.3	1.4
Emission factor, g/kg		0.037	0.087

Note: Blank indicates particulate emissions not reported.

Emissions from a drum dryer were reported in the National Emission Data System (NEDS).[11] Annual emissions were given as 5.4 metric tons and the production rate was 0.9 metric tons/hr. The emission factor, assuming continuous operation, is 0.7 g/kg.

One company reported that uncontrolled emissions from a rotary dryer ranged from 5 g/kg to 10 g/kg before installation of a baghouse. Opacity ranged from 20% to 30%. The emission factor with the baghouse was 0.25 g/kg (>95% efficiency), and the opacity reading was 0%.

Because of the wide range in emission factors, the diversity in dryers and calciners, the limited data, and the unknown accuracy of the data, an average emission factor was not determined for particulates. Instead, a range of emission

[11]Point Source Listing for Inorganic Pigments, SSC 3-01-035, National Emission Data System. Environmental Protection Agency. Research Triangle Park. August 1974.

factors for uncontrolled emissions, from 0.04 g/kg to 10 g/kg, is used to describe particulate emissions. Controlled emissions are on the order of <0.25 g/kg. The actual lower limit is unknown since only one baghouse effluent has been tested.

Barium sulfate dryers were not studied because the compound is not hazardous and the amount of material processed is only $\sim 5.0 \times 10^3$ metric tons/yr. Based on a worst case emission factor of 10 g/kg, total particulate emissions would be 50 metric tons/yr.

6. Emissions from Packaging and Shipping

After barium compounds have been dried, they may be screened and milled before packaging. All of these steps in final product preparation occur within the plant building and are not sources of fugitive emissions.

The loading of bulk product into railroad hopper cars may cause dusting. However, observation of a loading operation showed that the dust cloud was visible only at the top of the railroad car. No dust could be seen drifting away from the operation and it was concluded that emissions from this process were also zero.

Any other possible fugitive emissions were measured in the sampling tests discussed in Appendix C. They appear in the aggregate emission factor of 1 g/kg reported for barite preparation.

7. Summary

Emission factors and their associated accuracies are summarized in Table 15 for the entire production process. Both controlled and uncontrolled emission factors are presented where appropriate. Uncontrolled emissions from the black ash rotary kiln are controlled with cyclones, and uncontrolled dryers and calciners are equipped with cyclones or dust traps.

B. EMISSION CHARACTERISTICS

1. Barite Preparation

Barite ore is primarily (95%) barium sulfate, a nonhazardous chemical. The pure compound is used in taking x-ray photographs of the stomach and intestines. No Threshold Limit Value (TLV®) has been specifically assigned to $BaSO_4$ or barite.[12]

Inhalation of barite dust causes the lungs to appear dark on an x-ray photograph, a condition known as baritosis.

---

[12] TLV's® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists. Cincinnati. 1975. 97 p.

Table 15. SUMMARY OF EMISSION FACTORS

Process	Emission	Emission factor, g/kg			Basis for emission factor
		Uncontrolled	Controlled	Type control	
Barite preparation	Particulates	-[a]	1 ± 75%	Water spray	Feed material into the rotary kiln
Black ash (BaS) rotary kiln	Particulates	10 ± 50%	≤0.4	Scrubber (only particulates and SO_x are known to be controlled)	Feed material into the rotary kiln
	SO_x	25 ± 20%	≤0.5[b]		
	NO_x	0.6 ± 100%	0.6[b]		
	CO_x	5 ± 100%	5[b]		
	Hydrocarbons	0.8 ± 100%	0.8[b]		
	POM's	0.001 to 0.01	unknown		
H_2S incinerator	SO_x	1,882 ± 1%	-[a]	-[a]	H_2S burned
$Ba(OH)_2$ production Great Western Sugar rotary kiln	Particulates	-[a]	Assumed to be the same as black ash rotary kiln	Scrubber (only particulates and SO_x are known to be controlled)	Feed material into the rotary kiln
	SO_x	-[a]			
	NO_x	-[a]			
	CO_x	-[a]			
	Hydrocarbons	-[a]			
Sherwin-Williams proprietary	Particulates	-[a]	<0.5	Electrostatic precipitator (only particulates are controlled)	$Ba(OH)_2$ produced
	SO_x	410 ± 10%	-[a]		
	NO_x	0.8 ± 113%	-[a]		
	CO_x	0.11 ± 55%	-[a]		
	Hydrocarbons	0.07 ± 144%	-[a]		
Product dryers and calciners	Particulates (soluble barium compounds)	0.04 to 10	≤0.25	Baghouse	Product dryed or calcined

[a] Not applicable.

[b] Assumed to be the same as uncontrolled.

This condition has no specific symptoms and does not seem to reduce lung capacity or cause emphysema or bronchitis.[13-16]

2. Rotary Kiln and H_2S Incinerator

Emissions from the rotary kiln and H_2S incinerator consist of particulates, SO_x, NO_x, CO, hydrocarbons, and POM's. The emission characteristics are summarized in Table 16.

The health effects of airborne POM's have been the subject of much study, and it is suspected that these materials contribute to the higher incidence of disease in urban areas. Several of the POM's are known carcinogens when injected into experimental animals. However, because of the complex nature of the atmosphere, it is impossible to delineate the actual effects of airborne species.[8]

---

[13]Pendergrass, E. P., and R. R. Greening. Baritosis. Archives of Industrial Hygiene and Occupational Medicine. 7:44-48, 1953.

[14]Willson, J. K. V., P. S. Rubin, and T. M. McGee. The Effects of Barium Sulfate on the Lungs. American Journal of Roentgenology, Radium Therapy and Nuclear Medicine. 82:84-94, July 1959.

[15]Gleason, M. N., R. E. Gosselin, and H. C. Hodge. Clinical Toxicology of Commercial Products. Baltimore, The Williams & Wilkins Co., 1957. p. 28-29, 120-121.

[16]Barium and Its Inorganic Compounds. American Industrial Hygiene Association Journal. 23:517-518, November-December 1962.

Table 16. CHARACTERISTICS OF EMISSIONS FROM ROTARY KILNS AND H_2S INCINERATOR

Emission	TLV, mg/m^3	Ambient air quality standard, mg/m^3	Atmospheric reactivity	Health effects
Particulate	10	0.26	Stable	
SO_x	13 (SO_2)	0.365	Forms sulfates; contributes to photochemical smog	Irritating to lungs
NO_x	9 (NO_2)	0.1	Forms nitrates; contributes to photochemical smog	Irritating to lungs
CO	55	40	Stable	Asphyxiant
Hydrocarbons	(1,000 ppm, CH_4)	0.16	Reacts with acidic gases in the formation of photochemical smog	Methane is an asphyxiant
POM's	0.2	None	Oxidize readily in the atmosphere	Some POM's are carcinogenic

3. Dryers and Calciners

Particulates composed of soluble barium compounds are emitted during the drying and calcining of $BaCO_3$, $BaCl_2$ and $Ba(OH)_2$. These compounds are all considered hazardous on ingestion and have a TLV of 0.5 mg/m^3.[12,15]

The effects of barium poisoning are acute rather than chronic since barium compounds are not accumulated by the body. The first symptoms on ingestion are usually great weakness, salivation, and nausea, followed by vomiting, diarrhea, and severe abdominal pain. Later symptoms include

paralysis of the extremities, breathing difficulty, and rapid pulse. Eventually cyanosis sets in and then death.[6,15]

Effects on inhalation are a matter of speculation since no controlled studies have been performed. Occupational poisoning is practically unknown, and the few reported cases are ambiguous in terms of the actual cause of symptoms. Because these compounds are toxic on ingestion, it is recommended that exposure to airborne dusts be reduced to 0.5 mg/m^3.[12,16,17]

C. ENVIRONMENTAL EFFECTS

1. Total Emissions

In order to assess the environmental impact of barium chemical production, total national emissions of criteria pollutants from the industry were calculated. Each process causing emissions was treated separately by considering the material processed at each of the four major plant sites and the control techniques employed in each case.

a. Barite Preparation - Approximately 98% of raw material consumption occurs at three locations (Appendix A.1). One of these plants receives milled barite ore; the other two plants grind the ore on site. Fugitive dust from grinding is partially controlled at one site with water sprays and at the other site by partial enclosure of the operation and by use of a baghouse on the exhaust. The emission factor of 1 g/kg applies to grinding operations at both sites, and total particulate emissions are estimated at 78 metric tons/yr.

---

[17]Effect of Barium Carbonate Fumes on Respiratory Tract. Journal of the American Medical Association. 117:1221, 1941.

There are fewer fugitive dust emissions from the two other large barium chemical plants because one does no grinding while the other (Great Western Sugar) consumes only 2.7×10^3 metric tons/yr of raw materials. Estimated emissions are <9 metric tons/yr. Total emissions of fugitive dust from the whole industry are ∿90 metric tons/yr.

b. Rotary Kiln -

(1) Particulates - Uncontrolled kilns process about two-thirds of the barite ore consumed in the industry. (This will be reduced to about one-third after baghouses are installed at Chemical Products.) Total particulate emissions from these kilns are 7.8×10^2 metric tons/yr. Controlled emissions (based on a 95% efficiency) are estimated at 39 metric tons/yr and total industry emissions are ∿820 metric tons/yr.

(2) SO_x - Uncontrolled SO_x emissions amount to 1.86×10^3 metric tons/yr, whereas controlled emissions (based on an emission factor of 0.5 g/kg) equal 20 metric tons/yr for a total of 1.88×10^3 metric tons/yr.

(3) NO_x - No data are available on how well NO_x emissions are controlled by scrubbers. Therefore, based on an uncontrolled emission factor of 0.625 g/kg, total industry emissions amount to 73 metric tons/yr.

(4) CO and hydrocarbons - Carbon monoxide emissions total 550 metric tons/yr while hydrocarbons emissions amount to 90 metric tons/yr. Both figures are for uncontrolled emissions.

c. H_2S Incinerator - Two barium chemical plants operate H_2S incinerators. Total SO_x emissions from the two inciner-

ators were found by using NEDS data for one plant (SO_x calculated by a material balance), and using the average hourly SO_x emission rate for the other plant (as supplied by plant personnel). Total emissions are 3.3×10^3 metric tons/yr.

d. $Ba(OH)_2$ Production - Total emissions at Great Western Sugar are based on the controlled emission factors given in Table 15 for the black ash rotary kiln. The material fed into the kiln is greater than the estimated $Ba(OH)_2$ production (Appendix A.4) of 7×10^3 metric tons because of coproduction of $BaSiO_3$ and stack losses (SO_2 and CO_2). The feed is estimated at 1.4×10^4 metric tons/yr, and annual emissions are therefore: particulates, 5 metric tons/yr; SO_x, 7 metric tons/yr; NO_x, 8 metric tons/yr; CO, 68 metric tons/yr; and hydrocarbons, 10 metric tons/yr.

Total emissions at Sherwin-Williams, based on the emission factors in Table 15 and production of 5.5×10^3 metric tons/yr of $Ba(OH)_2$ (Appendix A.4), are: particulates, 3 metric tons/yr; SO_x, 2.045×10^3 metric tons/yr; NO_x, 4 metric tons/yr; CO, <1 metric ton/yr, and hydrocarbons, <0.4 metric tons/yr.

e. Dryers and Calciners - The compounds $BaCO_3$, $BaCl_2$, and $Ba(OH)_2$ are dried except for the $Ba(OH)_2$ produced by Great Western Sugar Co., and about one-third of the $BaCO_3$ made is calcined for use in glass manufacturing. The industry utilizes seven dryers and three calciners, of which three dryers and one calciner are controlled with baghouses, and one dryer is controlled with a wet scrubber. The amounts of products dried and calcined are shown in Table 17.

Table 17. BARIUM COMPOUNDS DRIED AND CALCINED ANNUALLY

Products dried and calcined	Controlled, metric tons	Uncontrolled,[a] metric tons	Total,[b] metric tons
$BaCO_3$	31,900	21,300[c]	53,200
$BaCl_2$	0	9,000	9,000
$Ba(OH)_2$	5,000	0	5,000
Total	36,900	30,300	67,200

[a]These are equipped with cyclones or settling chambers.
[b]See Appendix A.
[c]Includes one predryer.

Total particulate emissions were calculated, based on an uncontrolled emission factor of 5 g/kg and a controlled emission factor of 0.25 g/kg, to be 160 metric tons/yr. This value may be high because the industry has installed controls preferentially on the dustiest dryers.

f. Summary - Total emissions from the barium chemicals industry are summarized in Table 18.

Table 18. TOTAL EMISSIONS FROM BARIUM CHEMICALS INDUSTRY

Source	Particulates	SO_x	NO_x	CO	Hydrocarbons
Barite prep.	90	0	0	0	0
Rotary kiln	820	1,880	73	550	90
H_2S incinerator	0	3,200	0	0	0
$Ba(OH)_2$ prod.	8	2,050	12	69	11
Dryers and calciners	160	0	47[a]	6[a]	4[a]
Total	1,100	7,200	130	625	105

[a]From Appendix B.1.

The magnitude of these emissions can be compared to the total emissions from all stationary sources in the states of California, Colorado, Georgia, and Kansas[18] (Table 19). It can be seen that the barium chemicals industry contributes less than 1% of the emission burden from these four states for each criteria pollutant, and less than 0.1% of the national emission burden.

2. Source Severity

In addition to the total national emissions of criteria pollutants, another measure of the potential environmental effect of barium chemicals production is the ratio of the average maximum ground level concentration, $\bar{\chi}_{max}$, of a plant emission to the corresponding ambient air quality standard, AAQS. This ratio has been termed the source severity, S, as defined earlier in Equation 1:

$$S \equiv \frac{\bar{\chi}_{max}}{AAQS}$$

In the case of noncriteria pollutants a "reduced" TLV, called the hazard factor (F), replaces the AAQS, and source severity is defined as:

$$S \equiv \frac{\bar{\chi}_{max}}{F} \qquad (12)$$

where $$F = TLV \times 8/24 \times 1/100 \qquad (13)$$

8/24 corrects the TLV to a 24-hour exposure, and 1/100 is a safety factor.

Table 19. TOTAL EMISSIONS OF CRITERIA POLLUTANTS BY STATE AND NATION[18]

Location	Particulates, metric tons/yr	SO_x, metric tons/yr	NO_x, metric tons/yr	Hydrocarbons, metric tons/yr	CO metric tons/yr
California	1,006,452	393,326	1,663,139	2,160,710	8,237,667
Colorado	201,166	49,188	147,496	193,456	875,781
Georgia	404,574	472,418	379,817	458,010	2,036,010
Kansas	348,351	86,974	233,987	309,633	1,002,375
All four states	1,960,543	1,001,906	2,424,439	3,121,809	12,151,833
Total emissions from barium chemicals industry	1,100	7,200	130	625	105
Industry contribution to state total	0.056%	0.72%	<0.01%	<0.01%	<0.01%
United States	17,872,000	29,949,000	22,258,000	22,045,000	96,868,000
Industry contribution to national total	<0.01%	0.024%	<0.10%	<0.10%	<0.10%

Values for $\bar{\chi}_{max}$ can be predicted from plume dispersion equations. Under C class air stability the following relations apply:[19]

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_0}{t}\right) \quad (14)$$

$$\chi_{max} = \frac{2\,Q}{\pi e u H^2} \quad (15)$$

where χ_{max} = instantaneous (i.e., 3-min. average) maximum ground level concentration

t_0 = 3 min.

t = averaging time of interest for $\bar{\chi}_{max}$

Q = emission rate, g/s

H = effective stack height, m

u = wind speed, m/s (the national average of 4.5 m/s was used)

π = 3.14

e = 2.72

A 24-hour averaging time was used for non-criteria pollutants.

For ground level sources (H=0) the maximum ground level concentration occurs by definition at the plant boundary. In this case S is related to the average distance, D, from the emission point to the plant perimeter. Equations for S in terms of Q, H, and D are summarized in Table 20. Detailed derivations are presented in Appendix E.

[19]Turner, D. B. Workbook of Atmospheric Dispersion Estimates, 1970 Revision. U.S. Department of Health, Education and Welfare. Cincinnati. Public Health Service Publication No. 999-AP-26. May 1970. 84 p.

Table 20. EMISSION SEVERITY EQUATIONS

Emission	Severity equation
For elevated sources:	
Particulate	$S = \frac{70\ Q}{H^2}$
SO_x	$S = \frac{50\ Q}{H^2}$
NO_x	$S = \frac{315\ Q}{H^{2.1}}$
Hydrocarbon	$S = \frac{162\ Q}{H^2}$
CO	$S = \frac{0.78\ Q}{H^2}$
Other	$S = \frac{5.5\ Q}{TLV \cdot H^2}$
For ground level sources:	
Particulate	$S = \frac{4{,}020\ Q}{D^{1.81}}$

a. Barite Preparation - Barite preparation is a ground level source of emissions and the relevant parameters are Q and D. The emission rate is equal to the product of the emission factor, shown in Table 15, and the amount of raw material processed at a plant site. As shown in Appendix A.1., three plants each process $\sim 39 \times 10^3$ metric tons/yr of raw material (barite ore plus coal/coke) and account for ~98% of raw material consumption. Therefore, Q = 1 g/kg · 3.9×10^7 kg/yr · 1 yr/3.15×10^7 s = 1.24 g/s.

The value for D, calculated in Appendix F for the barium chemicals plant that was sampled, is 244 m. The corresponding source severity, S, is 0.238.

b. Black Ash Rotary Kiln - Kiln stack heights are listed in Table 21 and emission factors are shown in Table 15. Table 22 lists source severities based on a feed rate of $\sim 39 \times 10^3$ metric tons/yr, an average stack height of 32 m, and no emission controls. (Effect of plume rise is considered in Appendix G.)

Table 21. KILN STACK HEIGHTS FOR BLACK ASH ROTARY KILN[1-3] (meters)

Uncontrolled		Controlled	
	38		10 (small kiln)
	28		
	29		23
Average	32	Average	23

The emission rate is lower when an alkaline scrubber is used as a control device. Severities for this case are shown in Table 23.

Table 22. SOURCE SEVERITIES FOR EMISSIONS FROM BLACK ASH ROTARY KILN (WITHOUT EMISSION CONTROLS)

Emission	Q, g/s	S
Particulate	12.37	0.846
SO_x	30.92	1.51
NO_x	0.742	0.161
CO	6.18	0.00471
Hydrocarbon	0.989	0.156
POM	0.00124 to 0.0124	0.0333 to 0.333

Table 23. SOURCE SEVERITIES FOR EMISSIONS FROM BLACK ASH ROTARY KILN (WITH ALKALINE SCRUBBER)

Emission	Q, g/s	S
Particulate	0.495	0.0655
SO_x	0.247 to 0.618	0.0234 to 0.0585
NO_x	0.742	0.323
CO	6.18	0.00911
Hydrocarbon	0.989	0.303
POM	unknown	unknown

A stack height of 23 m was used in calculating S. The capacity of the smaller controlled kiln was about half that of the large one, and the severities (with a stack height of 10 m) would be about twice as great.

c. H_2S Incinerator - The two H_2S incinerators have stack heights of 38 m and 36 m.[1-3] The emission rate was calculated by assuming that the total national SO_2 emission of

3.265×10^3 metric tons was emitted continuously and in an equal amount by both stacks. On this basis Q = 51.8 g/s and the source severity is 1.89.

d. Dryers and Calciners - Stack heights for dryers and calciners are shown in Table 24. An average process weight was found by dividing the total material dryed and calcined (67.2×10^3 metric tons) by the total number of dryers and calciners (10). This yields an annual capacity of 6.7×10^3 metric tons. The source severity of particulate emissions was found from the equation

$$S = \frac{5.5\ Q}{TLV \cdot H^2} \qquad (16)$$

using the TLV for soluble barium compounds (0.5 mg/m^3). The results, given in Table 25 show the range of severities for uncontrolled and controlled emissions for an average stack height. (See Appendix G for the effect of plume rise.)

Table 24. STACK HEIGHTS FOR DRYERS AND CALCINERS[1-3] (meters)

Uncontrolled	Controlled
12.2	6.1
12.2	9.1
7.9	13.7
11.0	13.7
11.0	7.6
Average 10.9	Average 10.0

Table 25. SOURCE SEVERITIES FOR DRYERS AND CALCINERS

Type of dryer/ calciner	Emission factor, g/kg	Q, g/s	Stack height, m	Source severity
Uncontrolled	0.4 to 10	0.00854 to 2.13	10.9	0.791 to 197
Controlled	≤0.25	≤0.0534	10.0	≤5.87

e. Barium Hydroxide Production - Source severities for the two processes were calculated from the emission factors and annual capacities presented in Section IV.A.4 and IV.C.1.d. The stack height for the rotary kiln equipped with an alkaline scrubber at Great Western Sugar is ∿18.3 m.[4] The stack height at Sherwin-Williams is 45.7 m.[3] Source severity values are included in Table 26.

f. Summary - S and $\overline{\chi}_{max}$ values for emissions from all the process operations are summarized in Table 26.

3. Affected Population

The average ground level concentration, $\overline{\chi}$, of an emission will vary with the distance, x, from the emission point, as shown in Figure 9.

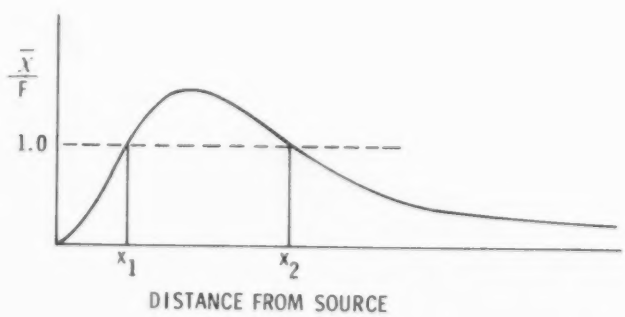


Figure 9. Variation of $\overline{\chi}$ with distance

Table 26. SUMMARY OF SOURCE SEVERITIES AND AVERAGE MAXIMUM GROUND LEVEL CONCENTRATIONS

Emission point	Emission	Stack height, m	Q, g/s	$\bar{X}_{max}$, $\mu g/m^3$	AAQS, mg/m^3	Source severity
Barite preparation	Particulate	0 (D = 244 m)	1.24	61.9	0.260	0.238
Black ash rotary kiln (uncontrolled)	Particulate	32	12.37	220	0.260	0.846
	SO_x	32	30.92	551	0.365	1.51
	NO_x	32	0.742	16.1	0.100	0.161
	CO	32	6.18	188	40	0.00471
	Hydrocarbons	32	0.989	25.0	0.160	0.156
	POM's	32	0.00124 to 0.0124	0.022 to 0.22	0.000667[a]	0.0333 to 0.333
Black ash rotary kiln (controlled)	Particulates	23	0.495	17.0	0.260	0.0655
	SO_x	23	0.247 to 0.618	8.5 to 21.4	0.365	0.0234 to 0.0585
	NO_x	23	0.742	32.3	0.100	0.323
	CO	23	6.18	364	40	0.00911
	Hydrocarbons	23	0.989	48.5	0.160	0.303
	POM's	23	unknown	unknown	0.000667[a]	unknown
H_2S Incinerator	SO_x	37	51.8	690	0.365	1.89
Dryers and calciners (uncontrolled)	Soluble barium compounds	10.9	0.00854 to 2.13	1.32 to 328	0.00167[a]	0.791 to 197
Dryers and calciners (controlled)	Soluble barium compounds	10.0	≤0.0534	≤9.78	0.00167[a]	≤5.87
Barium hydroxide production Sherwin-Williams	Particulate	45.7	0.0791	0.69	0.260	<0.01
	SO_x	45.7	64.87	567	0.365	1.55
	NO_x	45.7	0.127	1.30	0.100	0.013
	CO	45.7	0.0087	0.13	40	<0.01
	Hydrocarbons	45.7	0.0111	0.14	0.160	<0.01
Great Western Sugar	Particulates	18.3	0.173	9.38	0.260	0.036
	SO_x	18.3	0.216	11.8	0.365	0.032
	NO_x	18.3	0.259	18.2	0.100	0.182
	CO	18.3	2.16	201	40	<0.01
	Hydrocarbons	18.3	0.345	26.7	0.160	0.167

[a]Reduced TLV.

As a result, the population around a source site will be exposed to differing emission levels. The affected population is defined as the population around a site exposed to a $\bar{\chi}$/AAQS ratio greater than 1.0. (For noncriteria pollutants the ratio $\bar{\chi}$/F is used.) The mathematical derivation of the affected population is presented in Appendix E.

The affected population was calculated for the various emission points in the barium chemicals industry (Table 27). An average population density of 27 persons/km^2 was used (based on the four largest manufacturing sites), except for barium hydroxide production in which case the actual population densities at the two plant sites were used. Other input data (Q, h) were identical to those employed in the source severity calculations.

Since barite preparation is a ground level source (h = 0), the severity equation for particulates was solved to find the distance at which S = 1.0.

For particulates, $$S = \frac{4{,}020\ Q}{D^{1.81}}$$

Using Q = 1.24 g/s for barite preparation, and letting S = 1.0, then D = 110 m. Since the distance to the plant boundary is 244 m, the affected area is zero; i.e., no population is exposed to $S \geq 1.0$.

Table 27. SUMMARY OF AFFECTED POPULATION

Emission point	Emission	Stack height, m	Q, g/s	Population density, persons/km^2	Affected area, km^2	Affected population, persons
Barite preparation	Particulates	0 (D = 244 m)	1.24	27	0	0
Black ash rotary kiln (uncontrolled)	Particulate	32	12.37	27	0	0
	SO_x	32	30.92	27	1.3	35
	NO^x	32	0.742	27	0	0
	CO^x	32	6.18	27	0	0
	Hydrocarbons	32	0.989	27	0	0
	POM's	32	0.00124 to 0.0124	27	0	0
Black ash rotary kiln (controlled)	Particulate	23	0.495	27	0	0
	SO_x	23	0.247 to 0.618	27	0	0
	NO^x	23	0.742	27	0	0
	CO^x	23	6.18	27	0	0
	Hydrocarbons	23	0.989	27	0	0
	POM's	23	unknown	27	unknown	unknown
H_2S incinerator	SO_x	37	51.8	27	2.5	67
Dryers and calciners (uncontrolled)	Soluble barium compounds	10.9	0.00854 to 2.13	27	0 to 32.8	0 to 886
Dryers and calciners (controlled)	Soluble barium compounds	10.0	≤0.0534	27	0.6	18
Barium hydroxide production Sherwin-Williams	Particulate	45.7	0.0791	24	0	0
	SO_x	45.7	64.87	24	2.8	68
	NO^x	45.7	0.127	24	0	0
	CO^x	45.7	0.0087	24	0	0
	Hydrocarbons	45.7	0.0111	24	0	0
Barium hydroxide production Great Western Sugar	Particulate	18.3	0.173	8	0	0
	SO_x	18.3	0.216	8	0	0
	NO^x	18.3	0.259	8	0	0
	CO^x	18.3	2.16	8	0	0
	Hydrocarbons	18.3	0.345	8	0	0

SECTION V

CONTROL TECHNOLOGY

The production of barium chemicals involves a number of process steps that are potential sources of air pollution, and the industry employs a variety of techniques to reduce air emissions.

A. BARITE PREPARATION

The two companies that prepare barite on site use different particulate control techniques. One company has enclosed part of their operations and filters the exhaust air through a baghouse. The other company sprays the grinding operations with water. The emission factor in Section IV represents a controlled emission, and no data are available on control efficiencies. The discussion in the previous section showed that this process has a low environmental impact (S = 0.24).

B. BLACK ASH ROTARY KILN

Two of the five kilns in the industry are presently controlled with alkaline scrubbers and two are having baghouses installed. Plans are underway for placing a control device on the fifth kiln.[1-3] (The rotary kiln at Great Western Sugar, which produces tribarium silicate, is controlled with an alkaline scrubber.[4]) The scrubbers reduce both SO_x and

particulate emissions, while the baghouses control only particulates. The scrubbers may also lower the NO_x and hydrocarbon emissions, but no data are available.

Very little is known about the effect of control devices on POM emissions. Particulate POM's should be removed by the same devices (scrubbers, baghouses, electrostatic precipitators) that control other particulates.

The scrubber used by FMC Corporation has a double alkali scrubbing system (Figure 10). The unit consists of a vertical column packed with 9 feet of Intalox saddles and a wire mesh entrainment separator used in series. The absorbent liquor contains a high concentration of active alkali ($Na_2SO_3/NaHSO_3$) and sodium sulfate. Sulfate is formed by oxidation and dissolved in the liquor. Final separation is accomplished by a rotary vacuum filter which produces a waste product containing 50% moisture, $CaSO_3$, dissolved Na_2SO_4/Na_2SO_3, and kiln ash. SO_2 removal efficiency is up to 95% with simultaneous removal of kiln ash.[20]

The other scrubber system utilizes a packed tower with countercurrent flow. Control efficiencies have not been measured, but packed bed scrubbers typically achieve >90% control of SO_x and particulates.

---

[20]Kaplan, N. An EPA Overview of Sodium-Based Double Alkali Processes - Part II - Status of Technology and Description of Attractive Schemes. In: Proceedings: Flue Gas Desulfurization Symposium-1973. Environmental Protection Agency. Research Triangle Park. Publication No. EPA-650/2-73-038. December 1973. p. 1019-1060.

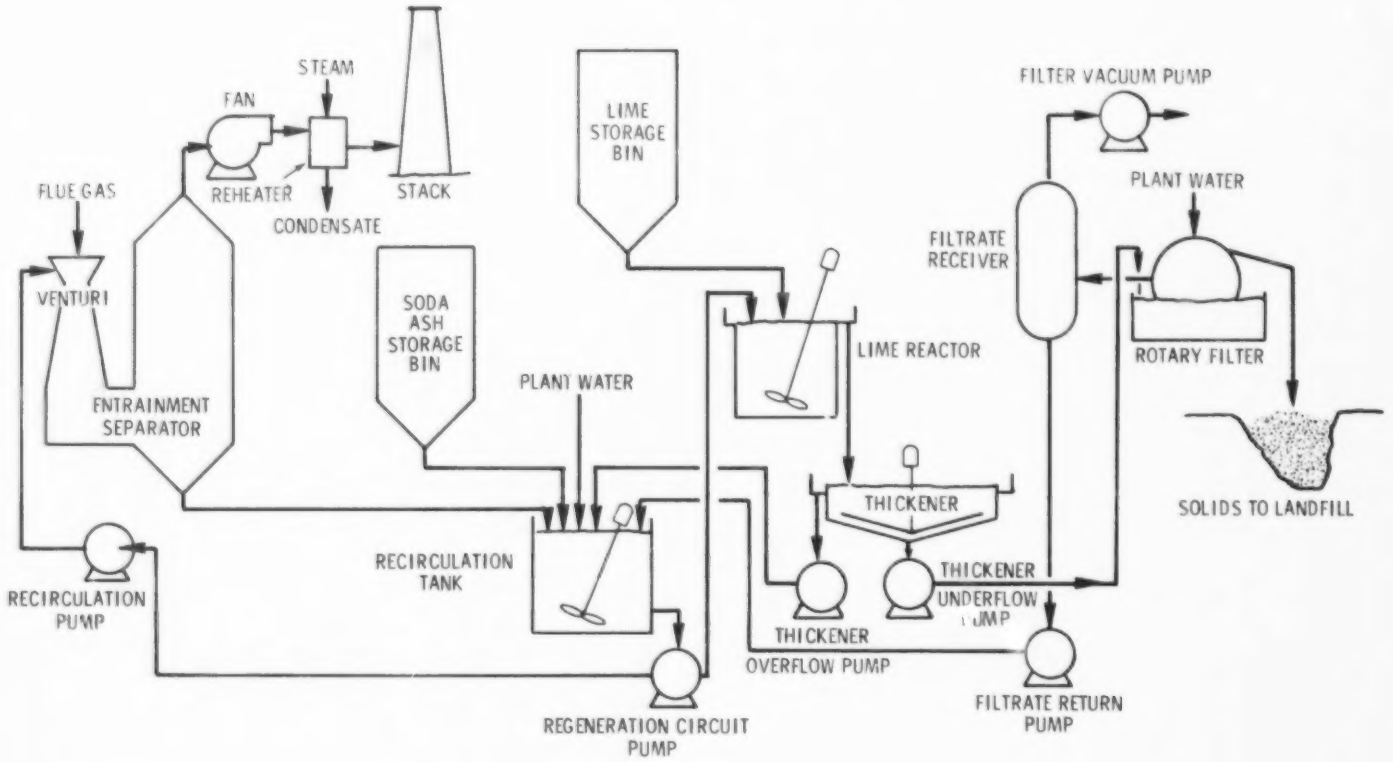


Figure 10. FMC double alkali scrubber system[19]

C. H_2S INCINERATOR

Hydrogen sulfide is generated when barium sulfide is reacted with CO_2 to make barium carbonate or with HCl to make barium chloride. One manufacturer uses Na_2CO_3 alone as a precipitating agent and so produces $BaCO_3$ and Na_2S instead of H_2S. This process modification eliminates any air pollution problem, and appears attractive as long as there is a market for the byproduct Na_2S.

In another process modification, the H_2S stream is absorbed in a bath of caustic instead of being incinerated. As in the previous process, Na_2S is a byproduct.

If hydrogen sulfide is not absorbed, it is incinerated to form SO_2. This is done to control the foul odor of H_2S since SO_2 actually has a lower TLV than H_2S (13 mg/m^3 vs 15 mg/m^3). No control devices are used to lower SO_2 emissions from the incinerator.

D. DRYERS AND CALCINERS

Dryers and calciners are equipped with settling chambers or cyclones to reduce particulate losses. A number of them (4 out of 10) are also equipped with baghouses, and one is controlled with a wet scrubber. Producers have installed baghouses preferentially on the dustiest stacks (i.e., those exceeding 20% opacity limits), so that all of the stacks are now reported to meet state standards.

One baghouse showed a collection efficiency of ~95%, which is below the 99% efficiency generally reported for fabric filters. It is possible that a small particulate size (<1 μm) contributed to the lower value, since barium carbonate is

produced as a powder with a range in particle size from 0.1 μm to 10 μm. Efficiencies of other baghouses in the industry have not been reported.

E. BARIUM HYDROXIDE PRODUCTION

Great Western Sugar Company uses an alkaline scrubber on their rotary kiln to control particulate and SO_x emissions, enabling them to meet state emission standards. The control efficiencies have not been reported. The scrubber is a moving-bed type in which mobile plastic spheres are retained between fixed trays.

Sherwin-Williams Company employs an electrostatic precipitator to control particulate emissions from their $Ba(OH)_2$ process. The efficiency is not known, but precipitators can operate at efficiencies of >99%. This unit does not control SO_x emissions.

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. TECHNOLOGY

Technology in the barium chemicals industry is stable, the only recent major development being the production of barium hydroxide by Sherwin-Williams by a new proprietary process. Other activity has centered on process refinements to increase product yield and purity. No new processes are foreseen, partly because the barium chemicals market has declined over the past 10 years.

B. INDUSTRY PRODUCTION TRENDS

The production of barium chemicals has suffered an overall decline since the mid sixties as indicated in Figure 11.[5,21-30]

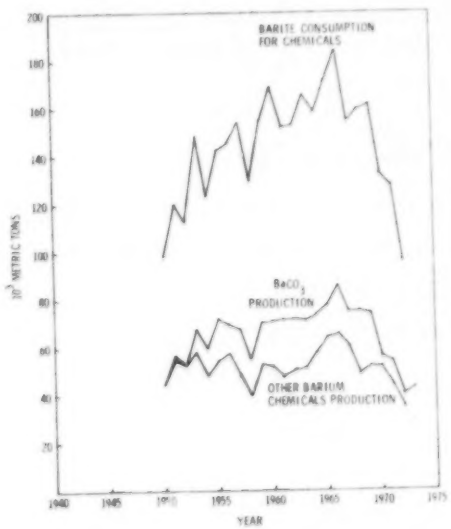


Figure 11. Production level of barium chemicals, 1950-1973[21-30]

[21]Arundale, J. C., and F. M. Barsigian. Barite. In: Minerals Yearbook 1951. Washington, Bureau of Mines, 1954. p. 186-195.

[22]Schreck, A. E., and J. M. Foley. Barite. In: Minerals Yearbook 1956, Volume I: Metals and Minerals. Washington, Bureau of Mines, 1958. p. 219-229.

[23]Skow, M. L., and V. R. Schreck. Barite. In: Minerals Yearbook 1961, Volume I: Metals and Minerals. Washington, Bureau of Mines, 1962. p. 295-308.

[24]Barite. In: Minerals Yearbook 1966, Volume I-II: Metals Minerals, and Fuels. Washington, Bureau of Mines, 1967. p. 428-433.

[25]Eilersten, D. E. Barite. In: Minerals Yearbook 1967, Volume I-II: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1968. p. 209-215.

[26]Diamond, W. G. Barite. In: Minerals Yearbook 1968, Volume I-II: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1969. p. 189-194.

[27]Diamond, W. G. Barite. In: Minerals Yearbook 1969, Volume I-II: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1971. p. 193-198.

[28]Fulkerson, F. B. Barite. In: Minerals Yearbook 1970, Volume I: Metals, Minerals, and Fuels. Washington, Bureau of Mines, 1972. p. 205-210.

[29]Fulkerson, F. B. Barite. In: Minerals Yearbook 1971, Volume I: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1973. p. 191-197.

[30]Current Industrial Report, Inorganic Chemicals 1973. Washington, U.S. Bureau of the Census, 1975. 28 p.

Data for 1974 and 1975 are not available, but production apparently continued to fall due to the economic slump. The decline in production is attributed to the replacement of barium compounds with materials of superior performance, and no improvement is forecast in the future.[31,32] As a result

[31]Chemical Profile: Barium Carbonate. Chemical Marketing Reporter. 207(13):9, March 31, 1975.

[32]Barium Chemical Producers See Future Demand Weakness. Chemical Marketing Reporter. 207(13):21, March 31, 1975.

air emissions in the industry are not expected to increase above current levels.

The major uses (>10% of the total, each) of barium carbonate are as a chemical intermediate in the production of other barium compounds, as an ingredient in glass making to increase optical density and radiation resistance, and as an additive in brick and ceramic manufacture that removes troublesome calcium and magnesium sulfates by coprecipitation.[6,31,32]

Barium chloride serves as a raw material in forming other barium pigments and as an ingredient in baths used to heat treat and case harden metals.[6]

As mentioned earlier, barium hydroxide is used in the refining of sugar from sugar beets. Great Western Sugar devotes their entire production to this purpose. The hydroxide also acts as a neutralizer in the manufacture of lubricating oil detergents composed of long-chain sulfonated hydrocarbons. The market in this area has decreased because the detergents for automobile use have changed to calcium hydroxide as a neutralizer. However, $Ba(OH)_2$ is still used in making compounds for trucks and heavy equipment.[3,6]

Although barium sulfate was once a common white pigment, it could not compete with titanium oxide and zinc oxide. It functions now as a pigment extender except for some special applications such as in photographic paper. In the area of medicine, barium sulfate plays a role as an x-ray contrast medium because its insolubility renders it nontoxic.[6] In this case, the compound must be purified to remove any traces of soluble barium or strontium salts.

Barium chemicals also have a variety of miscellaneous applications. However, at present there are no new uses which could spark an increase in production.

SECTION VII

APPENDIXES

A. Calculation of Production Data

B. Emission Calculations

C. Sampling Program

D. Polycyclic Organic Materials

E. Derivation of Source Severity Equations

F. Derivation of Average Distance from a Source to a Rectangular Plant Boundary

G. Plume Rise Correlation

Three standard and one modified Greenburg-Smith impingers were used in the system. The U-bend connecting the end of the absorbent trap to the first impinger was wrapped with asbestos to prevent premature condensation. The first impinger contained 100 ml of 10% KOH; the second and third each contained 100 ml of toluene; and the fourth, the modified Greenburg-Smith, contained 200 g of 6- to 16-mesh silica gel.

There were absolutely no greases used on any of the ball joints or other connections in the system. All ball joints were covered with Teflon, and extreme care was exercised to prevent loss of or damage to the Teflon.

The following steps were taken after sampling:

1. The Tenax trap was immediately removed from the system, its ends were capped and clamped, and it was placed in a plastic bag. (Parafilm "M" was used in place of the caps and clamps for 3 runs.) The bag was flattened to remove as much air as possible, flushed out with nitrogen and sealed, then placed under ice in an ice chest.

2. The filter was removed from its holder and carefully placed in the petri dish from which it came, and the top of the dish was loosely taped in place. The dish was placed in a plastic bag that was flattened to remove the air, then flushed with nitrogen, sealed, and placed under ice in an ice chest.

3. The first impinger was emptied into a properly labeled 250-ml amber bottle. The impinger was washed with methylene chloride and the wash added

to the impinger contents in the amber bottle. The bottle was then flushed with nitrogen, sealed, and placed under ice in an ice chest.

4. The contents of the other three impingers were treated as described in item 3, each in a separate bottle.

5. The entire train from the probe tip to the Tenax trap was rinsed with three portions of methylene chloride. The size of each portion was as small as possible. These three rinsings were placed in one amber bottle that was treated as described in item 3.

6. The samples were kept in a light-free enclosure at 0°C, under a nitrogen blanket.

The sampling site and number of traverse points were determined according to Method 1, Sample and Velocity Traverses for Stationary Sources.[34] The stack velocity, temperature and pressure were determined by Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate.[34] Stack gas composition was determined by Method 3, Gas Analysis for Carbon Dioxide, Excess Air and Dry Molecular Weight.[34]

The moisture was assumed to be 4%, based on data obtained during previous sampling by the company's sampling crew.

---

[34]Federal Register. 36(247):24876-24895, December 23, 1971.

The probe heater and oven heater were adjusted to provide a gas temperature approximately 14°C above the point at which moisture would condense out. Crushed ice was placed around the impingers to a level well above that of the solutions in the impingers. The oven temperature was held as close as possible to 50°C ±2°C, the ideal working temperature for Tenax.

Sampling runs were conducted according to Method 5, Determination of Particulate Emissions from Stationary Sources,[34] and the sampling train was leak checked by plugging the inlet to the filter holder and pulling a vacuum of 15 in. Hg, as stipulated in Method 5. For the sampling undertaken at this plant, runs 1 and 2 were done at a single point using the quartz filter. Runs 3 and 4 were carried out using a 12-point traverse with a regular glass fiber filter so that a particulate loading could also be obtained while POM's were being collected.

b. CO and Hydrocarbons

Carbon monoxide and hydrocarbon samples were taken using gas grab bottles. The grab bottles were evacuated and then the samples were drawn into them from the stack gas stream.

c. Fugitive Dust Sampling

Fugitive emissions were sampled with a GCA respirable dust monitor (Model RDM 101). The unit is a portable, self-contained monitoring device with automatic and direct digital readout of the mass concentration of airborne dust in mg/m^3. Eight samples were taken downwind of the source, and two samples were taken upwind of the source for reference. Although the testing was done specifically for the grinding

operation, dust emissions from other process operations may have increased the total amount of dust measured. Visual observation indicated that grinding was the major (>90%) source of fugitive dust at the plant.

Figure C-2 shows the approximate location of each sampling point in relation to the source at plant boundaries, and the predominant wind direction.

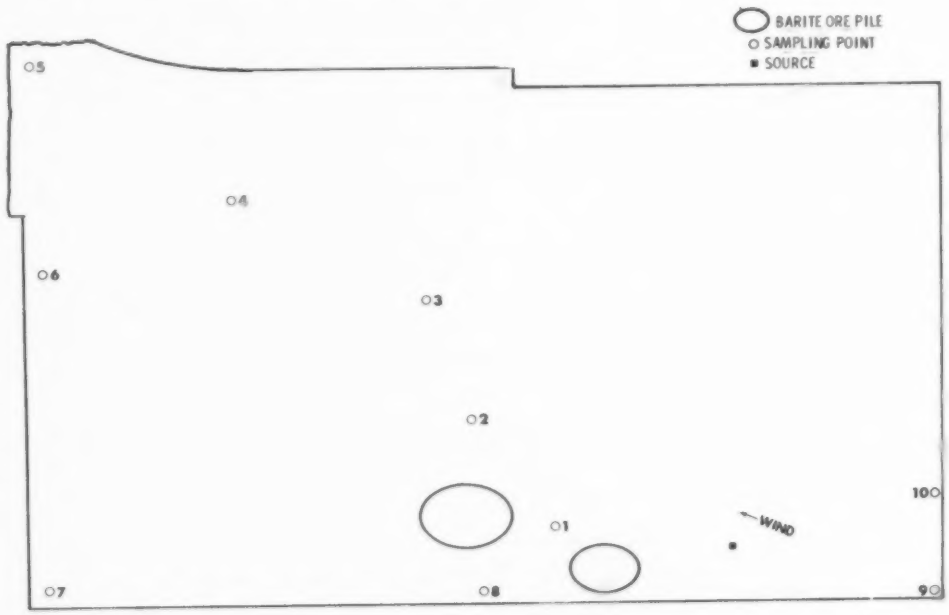
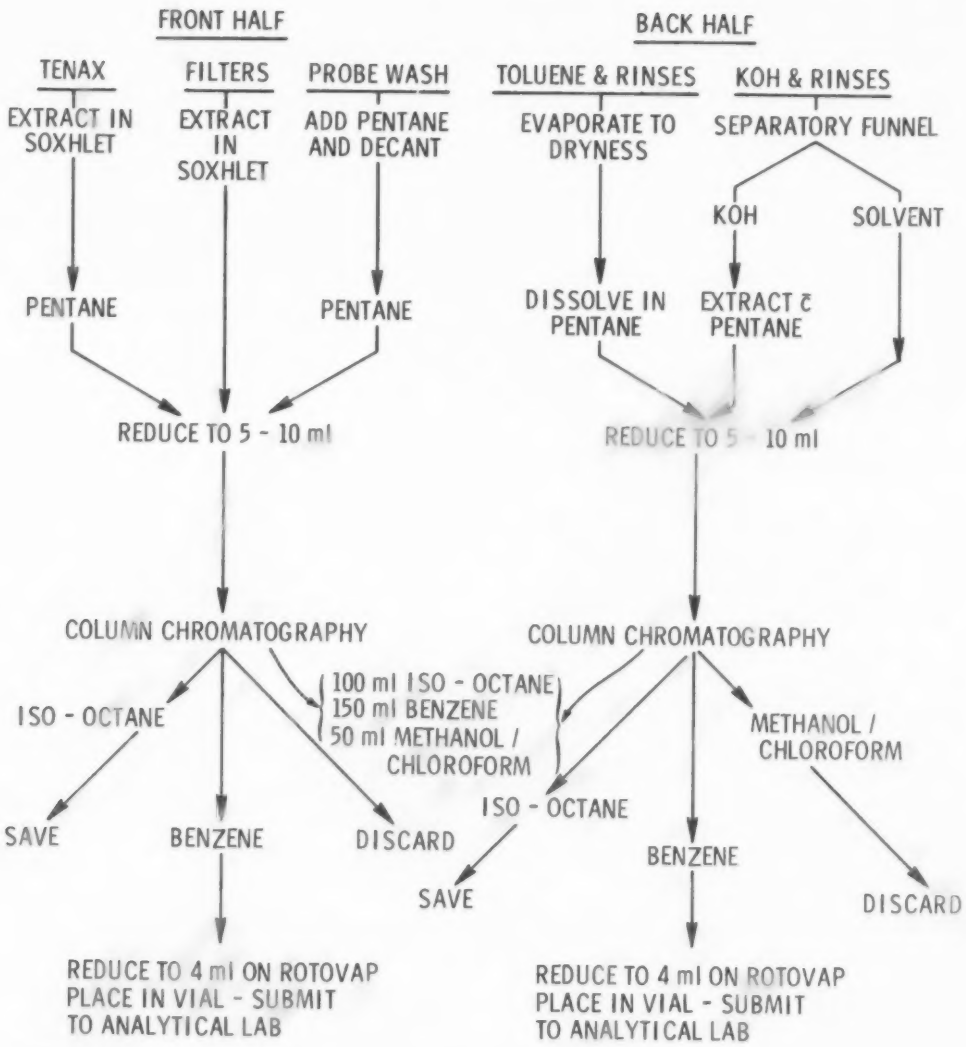


Figure C-2. GCA sampling locations

3. ANALYSIS OF SAMPLES

a. Particulate and POM Samples From the Rotary Kiln

(1) Preparative Procedure - Samples received from the field were kept refrigerated until they were analyzed. The samples consisted of several different impinger and wash solutions, Tenax, and filters. The fractions were worked up separately and then combined before final analysis. A flow diagram of the preparative procedure is shown in Figure C-3.



PRECAUTIONS

EXPOSE SAMPLES TO ONLY YELLOW LIGHT.
EXPOSE SAMPLES TO AS LITTLE OXYGEN AS POSSIBLE.
FLUSH SAMPLES WITH NITROGEN WHENEVER NECESSARY.
KEEP SAMPLES REFRIGERATED UNTIL WORK UP.
WRAP VIAL IN ALUMINUM FOIL TO PROTECT FROM LIGHT.
USE CHEMICALS "DISTILLED IN GLASS" WHENEVER POSSIBLE.
AVOID PHYSICAL CONTACT OF SAMPLE, ESPECIALLY IN CONCENTRATED STATE.
DO NOT USE A TOTAL VACUUM WHEN SAMPLE IS IN THE ROTOVAP.
USE NITROGEN RATHER THAN AIR IN THE ROTOVAP.

Figure C-3. POM sample work-up

The filters had been desiccated and weighed before the sampling effort. To measure the particulate collected in the four runs, they were again desiccated and weighed on an analytical balance, and the difference between the weights is the amount of particulate collected on the filters.

The solvent methylene chloride was used for the probe washes, which also contained particulate. Each wash was evaporated under nitrogen in a beaker that had been desiccated and weighed. The samples were also placed in a desiccator and then weighed, and the weight difference, again, is the amount of particulate collected.

For the POM work-up, the filters were placed in a thimble and extracted with 350 ml of pentane in a Soxhlet extraction apparatus. The Tenax was also placed in an extraction thimble and extracted with 350 ml of pentane. The particulate in the beakers was washed with pentane and the pentane decanted off to separate the soluble material from the insoluble particulate. These three pentane fractions were combined to make the front half sample.

The toluene portion from the impingers was evaporated to dryness in a rotovap. The residue was taken back up in pentane. The KOH solution from the impingers was placed in a separatory funnel and the aqueous portion was separated from the solvent. The KOH was extracted with three portions of pentane. The pentane with the toluene residue, the methylene chloride from the KOH separation, and the pentane from the extraction were combined and labeled as the back half sample.

(a) Runs 1 and 4 - The front and back half samples from runs 1 and 4 were each divided quantitatively into two parts; one of each was then sent to Battelle Memorial Institute's (BMI) Columbus Laboratory for analysis. The remaining

portions were retained and analyzed at Monsanto Research Corporation.

Each of the four samples was reduced on a rotovap to ∿5 ml total volume and then processed by Rosen chromatography. Each sample was put on a column of silica gel and eluted with a 100-ml portion of isooctane and a 150-ml portion of benzene. The benzene portion was again reduced to ∿5 ml in the rotovap. This fraction was transferred to a Kuderna-Danish flask and evaporated to dryness using a stream of N_2. The POM's were then redissolved in 2 ml of methylene chloride and transferred to a Viton-septum sealed vial. The vial was covered with aluminum foil and refrigerated until required for analysis. Just prior to analysis, the sample underwent one more volume reduction via the Kuderna-Danish method. The final volume was ∿500 µl, the volume size that seems to be optimum for detecting the POM peaks.

(b) Runs 2 and 3 - All four fractions of runs 2 and 3 were combined and this sample was sent to Battelle Memorial Institute (BMI) for work-up and analysis. The concentrated solution was then returned and the gas chromatographic-mass spectrometric analysis of this sample was also performed at MRC. This procedure was followed because the analysis of runs 1 and 4 indicated low POM levels in run 4. Since the sampling time for run 1 was about twice that for the other three runs, samples 2 and 3 were combined for better resolution.

(2) Analysis - Analysis of the POM's was performed on the Hewlett-Packard 5980A gas chromatograph-mass spectrometer (GC-MS) with computer-data system. The gas chromatographic separation was achieved using a 6-ft Dexil 300 glass column with temperature programming from 180°C to 280°C at 8°C/min,

becoming isothermal at 280°C. The carrier gas was helium at a flow rate of 30 ml/min.

The mass spectrometer, operating in the electron impact mode, was programmed to scan the 75-350 AMU range as the POM components eluted from the gas chromatograph. The data system was used to reconstruct the chromatogram using the total ion mode, while the individual POM mass ions were displayed using the selected ion mode. This provided the ability to identify POM's by their mass spectra and retention times and to quantitate the POM's by using the peak area of their mass ions. Figure C-4 shows the computer printout for a solution of standards.

Calibration curves were preprared for each POM of interest using varying concentrations of the POM standards in methylene chloride, plotting mass ion peak area vs. concentration, and determining response factors if linear. POM peaks in samples were compared with standard curves that had been obtained under the same attenuation, injection volume (2 µl), and tuning conditions.

BMI followed a similar analytical procedure with the samples sent to them; however, they utilized internal standards (methyl and phenyl anthracene derivatives) introduced into the samples prior to processing via a modified Rosen chromatographic separation. Quantitation was attained by relating response factors to the internal standards compared with a monthly calibration with POM standards. For runs 1 and 4, the front and back half samples were combined before analysis.

b. Carbon Monoxide and Hydrocarbons from the Rotary Kiln

Gas samples were analyzed on an F&M Model 810 hydrocarbon analyzer equipped with an Infrotronics Model CRS-101 inte-

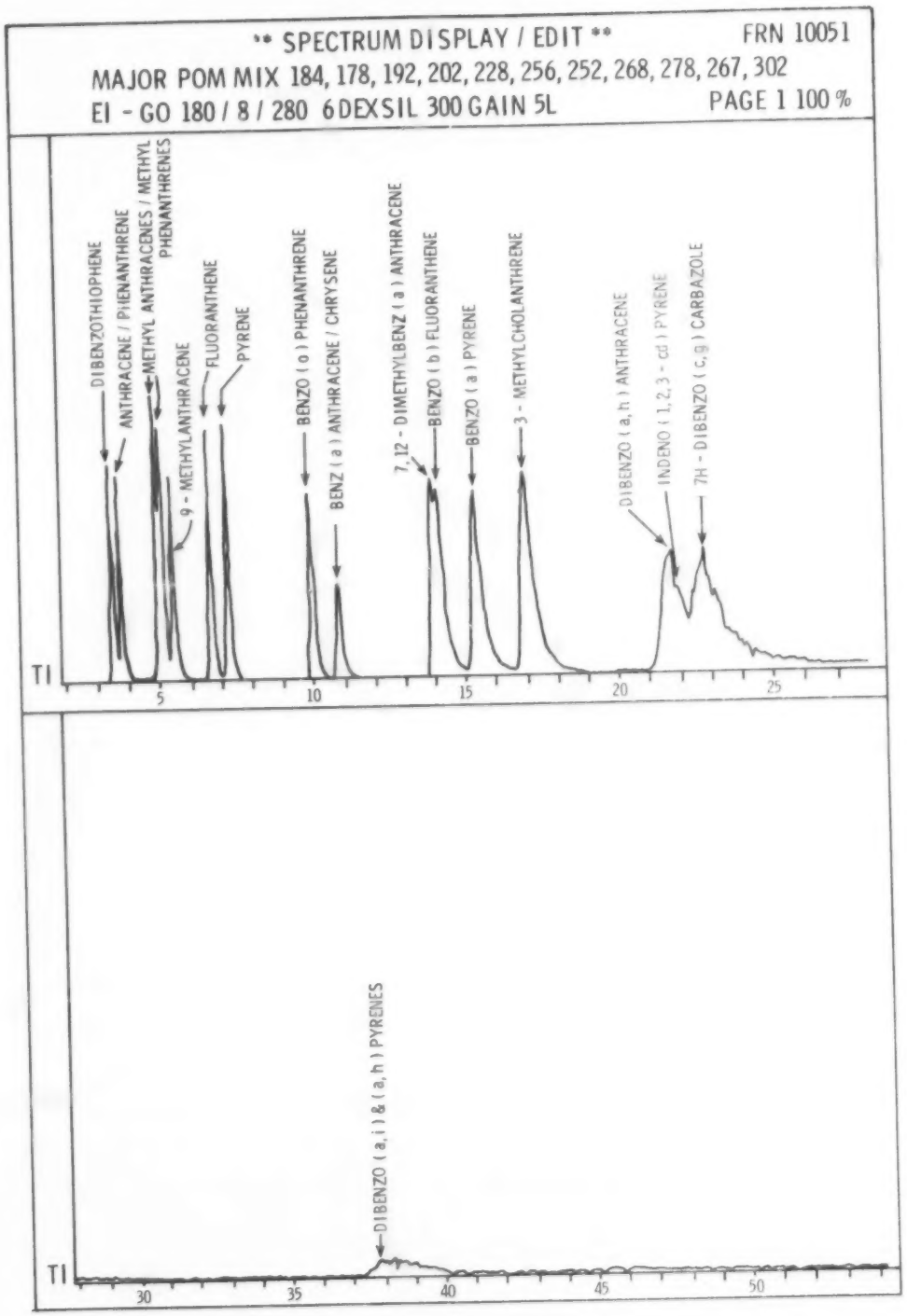


Figure C-4. Mass spectra for solution of standards for use in POM analyses

grator, using helium carrier gas and flame ionization detector. An unpacked 6 ft x 1/4 in. delay column was used with a 5 in. x 1/16 in. capillary restrictor. Concentrations were calculated by comparing peak area to calibration standards.

4. CALCULATIONS AND RESULTS

a. Particulates from the Rotary Kiln

Data from the four sampling runs are presented in Table C-1. The feed rate into the kiln was 150 lb/min, giving an average emission factor of 12.5 lb/ton (±15%).

b. POM's from the Rotary Kiln

The polynuclear organic compounds detected by GC-MS are listed in Table C-2. Structural formulas are given in Appendix D. The MRC analysis of runs 1 and 4 showed that over 95% of the POM's were in the front half of the sampling train, and the table gives data only from these analyses. The front and back halves of run 1 were later combined and rerun.

Emission rates and emission factors for each run are presented in Table C-3. Rates were calculated from the particulate data in Table C-1. Thus, for anthracene/phenanthrene in run 1, BMI measured 25,000 ng, or 25 µg. Since the original sample had been split in two, the total weight would be 50 µg. From Table C-1, a particulate weight of 976.75 mg corresponded to an emission rate of 56.058 lb/hr.

It follows that:

$$\frac{976.75 \text{ mg}}{56.058 \text{ lb/hr}} \Rightarrow \frac{1 \text{ µg}}{26.0327 \text{ mg/hr}}$$

Table C-1. PARTICULATE DATA

ABBR	DESCRIPTION	UNITS	1	2	3	4
TT	DURATION OF RUN	MINUTES	60.0	36.0	30.0	30.0
PB	BAROMETRIC PRESSURE	IN HG	29.66	29.50	29.50	29.50
DELH	AVG ORIFICE PRESS DROP	IN H2O	0.974	1.179	0.913	0.828
VM	VOL DRY GAS(METER CON.)	DCF	34.120	19.770	15.797	14.766
TM	AVG GAS METER TEMP	DEG F	114.0	93.0	100.7	104.7
VMSTD	VOL DRY GAS (STD COND)	DSCF	31.28	18.72	14.74	13.68
VW	TOTAL H2O COLLECTED	ML	27.4	16.4	12.9	12.0
VWG	VOL H2O VAPOR(STD CON)	SCF	1.301	0.778	0.613	0.569
PCNTM	PERCNT MOISTURE BY VOL		3.99	3.99	3.99	4.00
MD	MOLE FRACTION DRY GAS		0.960	0.960	0.960	0.960
CO2	PERCENT CO2		1.5	1.5	1.5	1.5
O2	PERCENT O2		19.2	19.2	19.2	19.2
N2	PERCENT N2		79.3	79.3	79.3	79.3
MWD	MOL WT OF DRY GAS		29.0	29.0	29.0	29.0
MW	MOL WT OF STACK GAS		28.6	28.6	28.6	28.6
DELP	AVG STACK VELOCITY HEAD	IN H2O	0.369	0.447	0.344	0.328
TS	STACK TEMPERATURE	DEG F	363.	380.	343.	350.
PM	STACK PRESSURE(STATIC)	IN H2O	-0.20	-0.20	-0.20	-0.20
PS	STACK PRESSURE (ABS)	IN HG	29.65	29.49	29.49	29.49
VS	AVG STACK GAS VELOCITY	FPM	2611.	2912.	2476.	2420.
DS	STACK DIAMETER	INCHES	39.50	39.50	39.50	39.50
AS	STACK AREA	SQ IN	1225.4	1225.4	1225.4	1225.4
QS	STACK FLOW RT(DRY STD)	DSCFM	13602.	14784.	13157.	12744.
QA	STACK FLOW RT(ACTUAL)	ACFM	22212.	24776.	21066.	20594.
DN	PROBE TIP DIAMETER	INCHES	0.245	0.245	0.245	0.245
PCTI	PERCENT ISOKINETIC		99.7	91.5	97.2	93.1
MF	PARTICULATE (FRONT)	MG	976.70	616.90	425.70	439.30
MT	PARTICULATE (TOTAL)	MG	976.75	616.90	425.70	439.30
CAN	PARTICULATE (FRONT)	GR/DSCF	0.4809	0.5074	0.4447	0.4945
CAO	PARTICULATE (TOTAL)	GR/DSCF	0.4809	0.5074	0.4447	0.4945
CAT	PARTICULATE (FRONT)	GR/ACF	0.2942	0.3025	0.2775	0.3058
CAU	PARTICULATE (TOTAL)	GR/ACF	0.2942	0.3025	0.2775	0.3058
CAW	PARTICULATE (FRONT)	LB/HR	56.055	64.292	50.137	54.010
CAX	PARTICULATE (TOTAL)	LB/HR	56.058	64.292	50.137	54.010

Table C-2. POM CONTENT OF SAMPLES (nanograms)

Compound	Barium run 1			Barium run 4		Barium runs 2 and 3	
	MRC[a]	MRC rerun	BMI	MRC[a]	BMI	MRC	BMI
Dibenzothiophene	190,000	170,700	-[b]	19,000	-[b]	99,500	-[b]
Anthracene/phenanthrene	350,000	310,100	25,000	37,500	22,000	233,000	325,800
Methylanthracene/methylphenanthrene	-[c]	52,400	7,800	-[c]	6,700	42,100	60,850
Fluoranthene	-[c]	31,400	3,500	-[c]	3,500	47,900	77,250
Pyrene	-[c]	12,800	1,600	-[c]	1,800	21,900	34,200
Methylpyrene/methylfluoranthene	-[c]	-[c]	1,500	-[d]	900	-[c]	11,550
Benzo(c)phenanthrene	<4,600[e]	3,300	<100[e]	<900[e]	<100[e]	<500[e]	2,000
Naphthobenzothiophene	-[c]	-[c]	-[b]	-[c]	-[b]	-[c]	-[b]
Chrysene/benz(a)anthracene	42,550	46,200	22,000	7,400	4,200	43,300	51,200
Methylchrysenes	-[c]	-[c]	2,300	-[c]	400	-[d]	16,650
7,12-Dimethylbenz(a)anthracene	<12,500[e]	1,000	-[b]	<2,500[e]	-[b]	<500[e]	-[b]
Benzofluoranthene	-[c]	34,100	7,700	-[c]	3,000	-[c]	19,900
Benzo(a)pyrene	[5,250[f] -[f] -[f]]	[6,500[f] -[f] -[f]]	800	[2,300[f] -[f] -[f]]	400	[9,900[f] -[f] -[f]]	[10,000[g] -[g]]
Benzo(e)pyrene			1,600		600		
Perylene			200		100		<2,000[e]
3-Methylcholanthrene	<2,100[e]	1,900	2,800	<200[e]	<100[e]	<500[e]	5,100
Indeno(1,2,3-cd)pyrene	<3,200[e]	4,800	2,000	1,750	<100[e]	7,100	2,050
Benzo(g,h,i)perylene	-[d]	-[d]	600	-[d]	<100[e]	-[d]	2,150
Dibenz(a,h)anthracene	<1,600[e]	4,400	4,800	2,300	<100[e]	3,950	<2,000[e]
7H-Dibenzo(c,g)carbazole	<3,200[e]	1,800	<100[e]	<300[e]	<100[e]	<500[e]	<2,000[e]
Dibenzo(a,i)&(a,h)pyrene	<7,900[e]	3,500	1,500	<750[e]	<100[e]	<500[e]	<2,000[e]
Coronene	-[d]	-[d]	<100[e]	-[d]	<100[e]	-[d]	<2,000[e]

[a] MRC of front half of sampling train only.

[b] Not determined.

[c] No standard available but mass ion possible for compound is detected.

[d] No standard available; possible mass ion not detected.

[e] No mass ion for compound is detected; detection limits given.

[f] Total not resolved; combined value for benzo(a)pyrene, benzo(e)pyrene and perylene.

[g] Combined value for benzo(a)pyrene and benzo(e)pyrene.

Table C-3. EMISSION RATES AND EMISSION FACTORS

Compound	Run 1					
	Emission rate, mg/hr			Emission factor, mg/kg		
	MRC	MRC rerun	BMI	MRC	MRC rerun	BMI
Dibenzothiophene	9,892	8,888	-[a]	2.423	2.177	-[a]
Anthracene/phenanthrene	18,223	16,145	1,302	4.464	3.955	0.319
Methylanthracene/methylphenanthrene	-[a]	2,728	406	-[a]	0.668	0.0995
Fluoranthene	-[a]	1,635	182	-[a]	0.400	0.0446
Pyrene	-[a]	666	83.3	-[a]	0.163	0.0204
Methylpyrene/methylfluoranthene	-[a]	-[a]	78.1	-[a]	-[a]	0.0191
Benzo(c)phenanthrene	<240	172	<5	<0.0587	0.0421	<0.001
Naphthobenzothiophene	-[a]	-[a]	-[a]	-[a]	-[a]	-[a]
Chrysene/benz(a)anthracene	2,215	2,405	1,145	0.543	0.589	0.280
Methylchrysenes	-[a]	-[a]	120	-[a]	-[a]	0.0293
7,12-Dimethylbenz(a)anthracene	<651	52	-[a]	<0.159	0.0127	-[a]
Benzofluoranthene	-[a]	1,775	401	-[a]	0.435	0.0982
Benzo(a)pyrene	[273[b]	[338[b]	41.6	[0.0670[b]	[0.0829[b]	0.0102
Benzo(e)pyrene	-[b]	-[b]	83.3	-[b]	-[b]	0.0204
Perylene	-[b]]	-[b]]	10.4	-[b]]	-[b]]	0.0026
3-Methylcholanthrene	<109	98.9	146	<0.0268	0.0242	0.0357
Indeno(1,2,3-cd)pyrene	<167	250	104	<0.0408	0.0612	0.0255
Benzo(g,h,i)perylene	-[a]	-[a]	31.2	-[a]	-[a]	0.0076
Dibenz(a,h)anthracene	<83.3	229	250	<0.0204	0.0561	0.0612
7H-Dibenzo(c,g)carbazole	<167	93.7	<5	<0.0408	0.0230	<0.001
Dibenzo(a,i)&(a,h)pyrene	<390	182	78.1	<0.0957	0.0446	0.0191
Coronene	-[a]	-[a]	<5	-[a]	-[a]	<0.001
Totals	30,603	35,658	4,430	7.497	8.734	1.085

[a] Not determined; see Table C-2 for additional information

[b] Total not resolved; combined value for benzo(a)pyrene, benzo(e)pyrene and perylene.

Table C-3 (continued). EMISSION RATES AND EMISSION FACTORS

Compound	Run 4			
	Emission rate, mg/hr		Emission factor, mg/kg	
	MRC	BMI	MRC	BMI
Dibenzothiophene	2,119	-[a]	0.519	-[a]
Anthracene/phenanthrene	4,182	2,454	1.024	0.601
Methylanthracene/methylphenanthrene	-[a]	747	-[a]	0.183
Fluoranthene	-[a]	390	-[a]	0.0956
Pyrene	-[a]	201	-[a]	0.0492
Methylpyrene/methylfluoranthene	-[a]	100	-[a]	0.0246
Benzo(c)phenanthrene	<100	<11	<0.025	<0.003
Naphthobenzothiophene	-[a]	-[a]	-[a]	-[a]
Chrysene/benz(a)anthracene	825	468	0.202	0.115
Methylchrysenes	-[a]	44.6	-[a]	0.0109
7,12-Dimethylbenz(a)anthracene	<279	-[a]	<0.068	-[a]
Benzofluoranthene	-[a]	335	-[a]	0.0820
Benzo(a)pyrene	[256[b]]	44.6	[0.0628[b]]	0.0109
Benzo(e)pyrene	[-[b]]	66.9	[-[b]]	0.0164
Perylene	[-[b]]	11.1	[-[b]]	0.0027
3-Methylcholanthrene	<22	<11	<0.0055	<0.003
Indeno(1,2,3-cd)pyrene	195	<11	0.0478	<0.003
Benzo(g,h,i)perylene	-[a]	<11	-[a]	<0.003
Dibenz(a,h)anthracene	256	<11	0.0628	<0.003
7H-Dibenzo(c,g)carbazole	<33	<11	<0.008	<0.003
Dibenzo(a,i)&(a,h)pyrene	<84	<11	<0.020	<0.003
Coronene	-[a]	<11	-[a]	<0.003
Totals	7,833	4,863	1.919	1.192

[a]Not determined; see Table C-2 for additional information.

[b]Total not resolved; combined value for benzo(a)pyrene, benzo(e)pyrene and perylene.

Table C-3 (continued). EMISSION RATES AND EMISSION FACTORS

Compound	Runs 2 and 3			
	Emission rate, mg/hr		Emission factor, mg/kg	
	MRC	BMI	MRC	BMI
Dibenzothiophene	2,477	-[a]	0.607	-[a]
Anthracene/phenanthrene	5,800	8,110	1.421	1.986
Methylanthracene/methylphenanthrene	1,048	1,515	0.257	0.371
Fluoranthene	1,192	1,923	0.292	0.471
Pyrene	545	851	0.134	0.208
Methylpyrene/methylfluoranthene	-[a]	287	-[a]	0.0704
Benzo(c)phenanthrene	<12.4	49.8	<0.0030	0.0122
Naphthobenzothiophene	-[a]	-[a]	-[a]	-[a]
Chrysene/benz(a)anthracene	1,078	1,274	0.264	0.312
Methylchrysenes	-[a]	414	-[a]	0.102
7,12-Dimethylbenz(a)anthracene	<12.4	-[a]	<0.0030	-[a]
Benzofluoranthene	-[a]	495	-[a]	0.121
Benzo(a)pyrene	[246[b]	[251[d]	[0.0604[b]	[0.0616[d]
Benzo(e)pyrene	-[b]	-[d]	-[b]	-[d]
Perylene	-[b]	<50	-[b]	<0.012
3-Methylcholanthrene	<12.4	127	<0.0030	0.0311
Indeno(1,2,3-cd)pyrene	177	51.0	0.0434	0.0125
Benzo(g,h,i)perylene	-[a]	53.5	-[a]	0.013
Dibenz(a,h)anthracene	98.3	<50	0.0241	<0.012
7H-Dibenzo(c,g)carbazole	<12.4	<50	<0.0030	<0.012
Dibenzo(a,i)&(a,h)pyrene	<12.4	<50	<0.0030	<0.012
Coronene	-[a]	<50	-[a]	<0.012
Totals	12,661[e]	15,348	3.102[e]	3.758

[a]Not determined; see Table C-2 for additional information.

[b]Total not resolved; combined value for benzo(a)pyrene, benzo(e)pyrene and perylene.

[d]Combined value for benzo(a)pyrene and benzo(e)pyrene.

[e]Values about 20% too low because a portion of the sample was consumed in analysis at BMI.

The emission rate for anthracene/phenanthrene is then 50 x 26.0327 = 1,300 mg/hr.

A comparison of results indicates major (order of magnitude) differences between runs although duplicate analyses (the two MRC tests on run 1 and the tests on runs 2 and 3) compare favorably (within a factor of 2). It appears that the preparative procedure is responsible for the differences in the MRC and BMI results for runs 1 and 4. The differences between the three tests may be caused by fluctuations in the stack gas and/or variations in the preparative technique.

Total POM emissions for each test are presented in Table C-4.

Table C-4. TOTAL POM EMISSIONS

Run	Test	Emission rate, g/hr	Emission factor, mg/kg
1	MRC (front)	30.6	7.5
	MRC rerun (front and back)	35.6	8.7
	BMI (both)	4.4	1.1
4	MRC (front)	7.8	1.9
	BMI (both)	4.9	1.2
2 & 3	MRC (front and back)	12.7[a]	3.1[a]
	BMI (both)	15.3	3.8

[a]Values about 20% low; see footnote to Table C-3.

APPENDIX D

POLYCYCLIC ORGANIC MATERIALS

The polycyclic organic materials (POM's) detected in samples from the black ash rotary kiln are listed in Table D-1 with their structural formulas and carcinogenicity. The standard nomenclature is used, but older synonymous names are also given, in parentheses. Starred (*) compounds indicate disagreement with standard numbering. The carcinogenicity of each compound is indicated by a simple code:[8]

- \- not carcinogenic
- ± uncertain or weakly carcinogenic
- \+ carcinogenic
- ++, +++, ++++ strongly carcinogenic

Table D-1. STRUCTURAL FORMULAS AND CARCINOGENICITY OF POM's

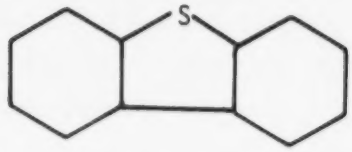
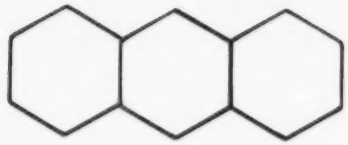
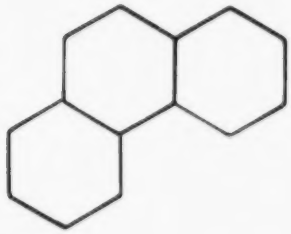
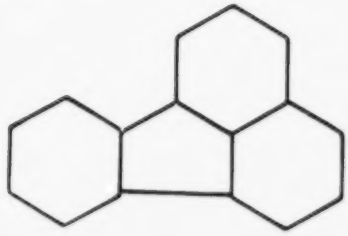
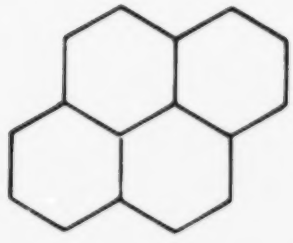
Compound	Structure	Carcinogenicity
Dibenzothiophene		-
Anthracene		-
Phenanthrene		-
Fluoranthene		-
Pyrene		-

Table D-1 (continued). STRUCTURAL FORMULAS AND CARCINOGENICITY OF POM's

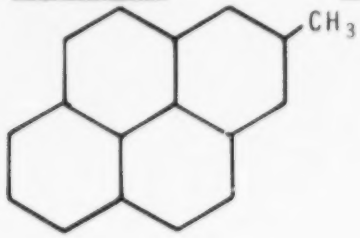
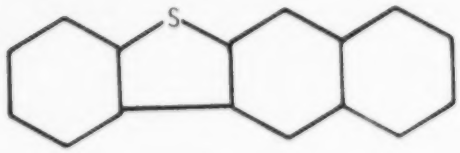
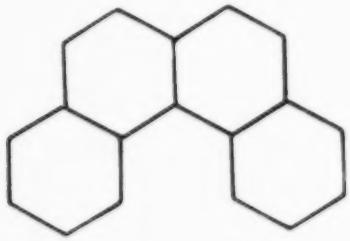
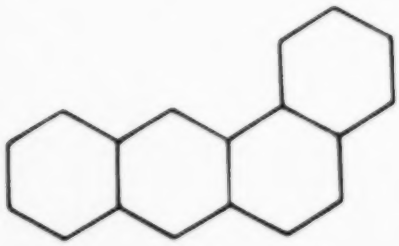
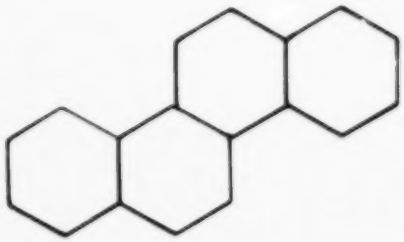
Compound	Structure	Carcinogenicity
Methylpyrene		-
Benzo-dibenzothiophene (Benzothionaphthene)		-
Benzo(c)phenanthrene (3,4-Benzophenanthrene)		+++
Benz(a)anthracene (1,2-Benzanthracene)		+
Chrysene (1,2-Benzophenanthrene)		±

Table D-1 (continued). STRUCTURAL FORMULAS AND CARCINOGENICITY OF POM's

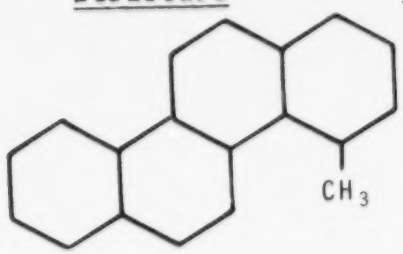
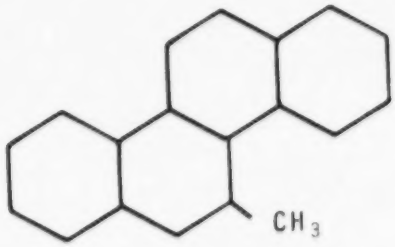
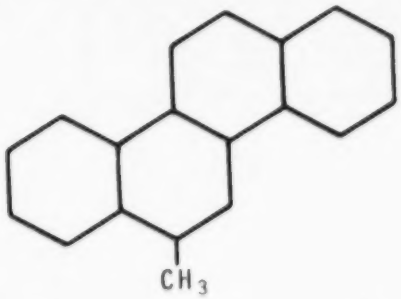
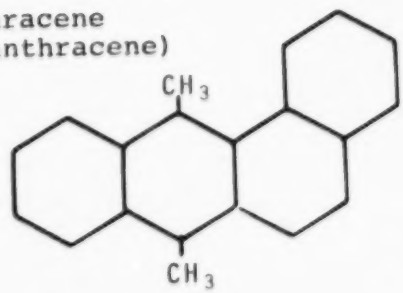
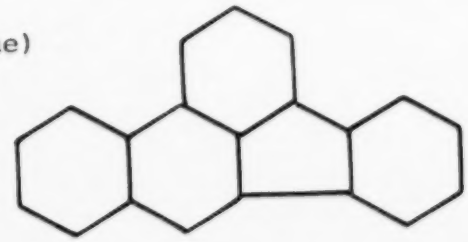
Compound	Structure	Carcinogenicity
4-Methylchrysene		±
5-Methylchrysene		±
6-Methylchrysene		±
7,12-Dimethylbenz(a)anthracene (9,10-Dimethyl-1,2-benzanthracene)		++++
Benzo(b)fluoranthene (2,3-Benzofluoranthene)		++

Table D-1 (continued). STRUCTURAL FORMULAS AND CARCINOGENICITY OF POM's

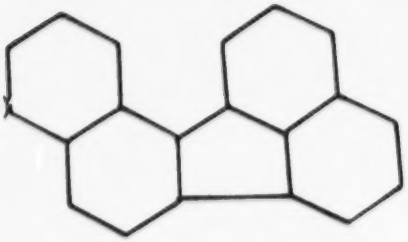
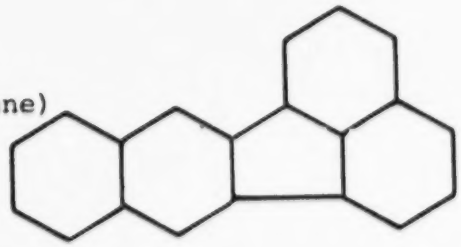
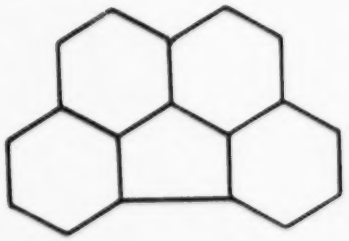
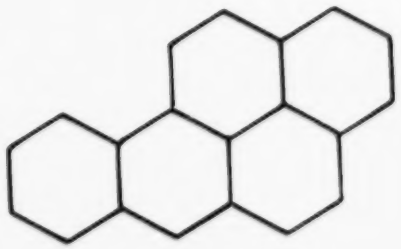
Compound	Structure	Carcinogenicity
Benzo(j)fluoranthene (7,8-Benzofluoranthene)		++
Benzo(k)fluoranthene (8,9-Benzofluoranthrene)		-
Benzo(ghi)fluoranthene		-
Benzo(a)pyrene (1,2-Benzopyrene) (3,4-Benzypyrene*)		+++

Table D-1 (continued). STRUCTURAL FORMULAS AND CARCINOGENICITY OF POM's

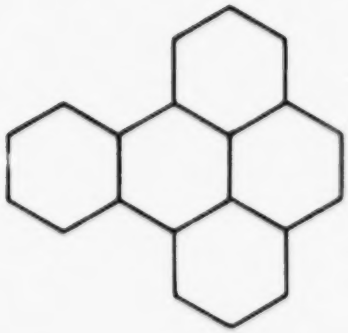
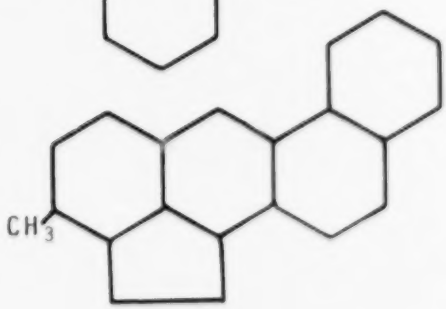
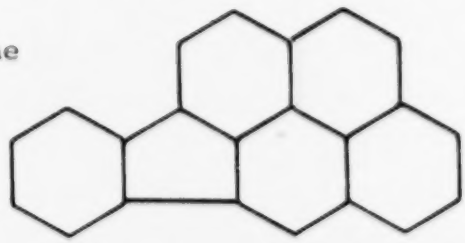
Compound	Structure	Carcinogenicity
Benzo(e)pyrene (4,5-Benzopyrene) (1,2-Benzopyrene*)		-
Perylene		-
3-Methylcholanthrene		++++
Indeno(1,2,3-cd)pyrene (o-Phenylenepyrene)		+

Table D-1 (continued). STRUCTURAL FOPMULAS AND CARCINOGENICITY OF POM's

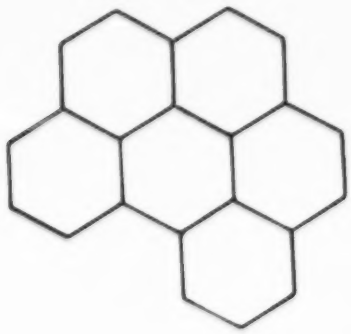
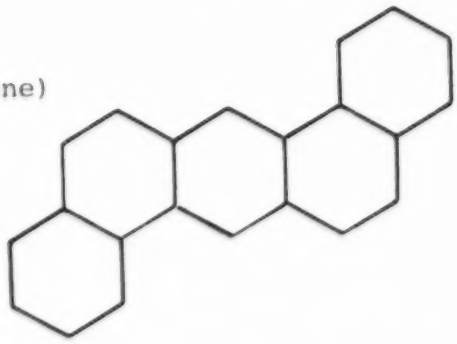
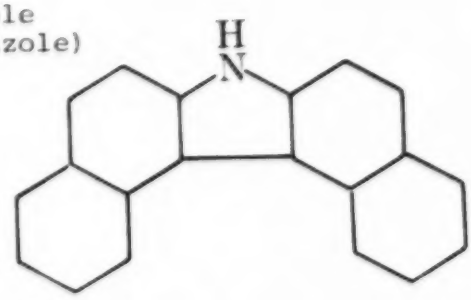
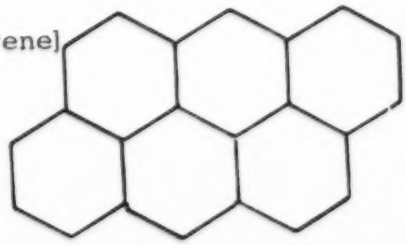
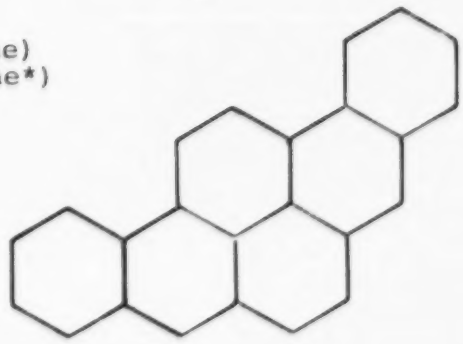
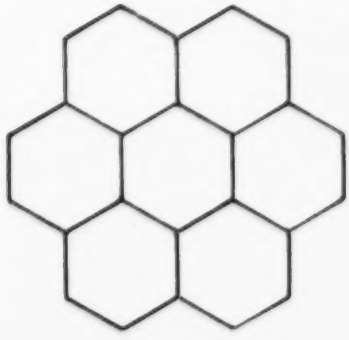
Compound	Structure	Carcinogenicity
Benzo(ghi)perylene		-
Dibenz(a,h)anthracene (1,2-5,6-Dibenzanthracene)		+++
Dibenzo(c,g)carbazole (3,4-5,6-Dibencarbazole)		+++
Anthanthrene [Dibenzo(cd,jk)pyrene]		-

Table D-1 (continued). STRUCTURAL FORMULAS AND CARCINOGENICITY OF POM's

Compound	Structure	Carcinogenicity
Dibenzo(a,h)pyrene (1,2-6,7-Dibenzopyrene) (3,4-8,9-Dibenzopyrene*)		+++
Dibenzo(a,i)pyrene (2,3-6,7-Dibenzopyrene) (4,5-8,9-Dibenzopyrene*)		+++
Coronene		-

APPENDIX E

DERIVATION OF SOURCE SEVERITY EQUATIONS
(T. R. Blackwood and E. C. Eimutis)

1. SUMMARY OF MAXIMUM SEVERITY EQUATIONS

The maximum severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, or the distance from the source to the nearest plant boundary, D, and the ambient air quality standard, AAQS, or the threshold limit value, TLV. The equations summarized in Table E-1 are developed in detail in this appendix.

Table E-1. POLLUTANT SEVERITY EQUATIONS

Pollutant	Severity equation
For elevated sources: Particulate	$\frac{70\ Q}{H^2}$
SO_x	$\frac{50\ Q}{H^2}$
NO_x	$\frac{315\ Q}{H^{2.1}}$
Hydrocarbon	$\frac{162\ Q}{H^2}$
CO	$\frac{0.78\ Q}{H^2}$
Other	$\frac{5.5\ Q}{TLV \cdot H^2}$
For ground level sources: Particulate	$\frac{4{,}020\ Q}{D^{1.81}}$

2. DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is:[18]

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(E-1)}$$

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3

Q = mass emission rate, g/s

σ_y = standard deviation of horizontal dispersion, m

σ_z = standard deviation of vertical dispersion, m

u = wind speed, m/s

y = horizontal distance from centerline of dispersion, m

H = height of emission release, m

x = downwind dispersion distance from source of emission release, m

π = 3.1416

We assume that χ_{max} occurs when $x >> 0$ and $y = 0$. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows:[35]

$$\sigma_y = ax^b \qquad \text{(E-2)}$$

$$\sigma_z = cx^d + f \qquad \text{(E-3)}$$

Values for a, b, c, d and f are given in Tables E-2 and E-3. Substituting these general equations into Equation E-1 yields:

---

[35]Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. (Presented at 61st Annual Meeting of the Air Pollution Control Association, for NAPCA, St. Paul, 1968.) 18 p.

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi ufx^{b}} \exp - \left[\frac{H^2}{2(cx^{d} + f)^2}\right] \qquad \text{(E-4)}$$

Assuming that χ_{max} occurs at x<100 m or the stability class is C, then f = 0 and Equation E-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}} \exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \qquad \text{(E-5)}$$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

so that Equation E-5 reduces to:

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^{2d}}\right] \qquad \text{(E-6)}$$

Table E-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a,36]

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a]For the equation

$$\sigma_y = ax^b$$

where x = downwind distance

b = 0.9031

[36]Tadmor, J. and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment. 3:688-689, 1969.

Table E-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a,35]

Usable range	Stability class	Coefficient		
		c_1	d_1	f_1
>1,000 m	A	0.00024	2.094	-9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2
100-1,000 m	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	f_3
<100 m	A	0.192	0.936	0
	B	0.156	0.922	0
	C	0.116	0.905	0
	D	0.079	0.881	0
	E	0.063	0.871	0
	F	0.053	0.814	0

[a]For the equation:

$$\sigma_z = cx^d + f$$

Taking the first derivative of Equation E-6

$$\frac{d\chi}{dx} = A_R \left\{ x^{-b-d} \left(\exp \left[B_R x^{-2d} \right] \right) \left(-2dB_R x^{-2d-1} \right) + \exp \left[B_R x^{-2d} \right] \left(-b-d \right) x^{-b-d-1} \right\} \quad \text{(E-7)}$$

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1} \left(\exp \left[B_R x^{-2d} \right] \right) \left[-2dB_R x^{-2d} - b - d \right] \quad \text{(E-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-2dB_R x^{-2d} - d - b = 0 \quad \text{(E-9)}$$

or

$$\left(b+d \right) x^{2d} = -2dB_R \quad \text{(E-10)}$$

or

$$x^{2d} = \frac{-2dB_R}{b+d} = \frac{2d\ H^2}{2c^2 (b+d)} \quad \text{(E-11)}$$

or

$$x^{2d} = \left(\frac{d\ H^2}{c^2 (b+d)} \right) \quad \text{(E-12)}$$

or

$$x = \left(\frac{d\ H^2}{c^2 (b+d)} \right)^{\frac{1}{2d}} \text{ at } \chi_{max} \quad \text{(E-13)}$$

Thus Equation E-2 and E-3 become:

$$\sigma_y = a \left(\frac{d\ H^2}{c^2 (d+b)} \right)^{\frac{b}{2d}} \quad \text{(E-14)}$$

$$\sigma_z = c \left(\frac{d\ H^2}{c^2 (b+d)} \right)^{\frac{d}{2d}} = \left(\frac{d\ H^2}{b+d} \right)^{\frac{1}{2}} \quad \text{(E-15)}$$

The maximum will be determined for U.S. average conditions of stability. According to Slade,[37] this is when $\sigma_y = \sigma_z$.

Since b = 0.9031, and upon inspection of Table E-2[36] under U.S. average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \leq d \leq 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d or:

$$\sigma_z = \frac{H}{\sqrt{2}} \qquad \text{(E-16)}$$

and

$$\sigma_y = \frac{a}{c}\frac{H}{\sqrt{2}} \qquad \text{(E-17)}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and a = c if b = d and f = 0 (between class C and D, but closer to belonging in class C).

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \qquad \text{(E-18)}$$

Substituting for σ_y and σ_z into Equation E-1 and letting y = 0:

$$\chi_{max} = \frac{2Q}{\pi u H^2} \exp\left[-\frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \qquad \text{(E-19)}$$

---

[a] The values given in Table E-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two.

- - - - - - - - - - -

[37] Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, Slade, D. A. (ed.). Oak Ridge, Tennessee, U.S. Atomic Energy Commission Technical Information Center. Publication No. TID-24190. July 1968. p. 113.

or

$$\chi_{max} = \frac{2\,Q}{\pi e u H^2} \qquad \text{(E-20)}$$

For ground level sources (H = 0), χ_{max} occurs by definition at the nearest plant boundary or public access. Since this occurs when y = 0, Equation E-1 becomes:

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \qquad \text{(E-21)}$$

From the foregoing analysis of U.S. average conditions, class C stability coefficients are the best first approximations to U.S. average conditions when $\sigma_y = \sigma_z$.

By letting D equal the distance to the occurrence of χ_{max} (see Tables E-2 and E-3),

$$\sigma_y = 0.209\ D^{0.9031} \qquad \text{(E-22)}$$

$$\sigma_z = 0.113\ D^{0.911} \qquad \text{(E-23)}$$

Thus, χ_{max} is determined as follows:

$$\chi_{max} = \frac{42.36\,Q}{\pi u D^{1.814}} \qquad \text{(E-24)}$$

It will be noted that Equations E-24 and E-20 are identical with the algebraic substitution of

$$H^2 = 0.01737\ D^{1.814} \qquad \text{(E-25)}$$

For U.S. average conditions u = 4.47 m/s so that Equation E-20 reduces to:

$$\chi_{max} = \frac{0.0524\,Q}{H^2} \qquad \text{(E-26)}$$

3. DEVELOPMENT OF SOURCE SEVERITY

The general source severity relationship has been defined as follows:

$$S = \frac{\bar{\chi}_{max}}{F} \qquad \text{(E-27)}$$

where S = source severity

$\bar{\chi}_{max}$ = average maximum ground level concentration

F = hazard factor

a. Noncriteria Emissions

The value of $\bar{\chi}_{max}$ may be derived from χ_{max}, an undefined "short term" concentration. An approximation for longer term concentration may be made as follows:[18]

For a 24 hour time period,

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{t_0}{t}\right)^{0.17} \qquad \text{(E-28)}$$

or

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3 \text{ minutes}}{1440 \text{ minutes}}\right)^{0.17} \qquad \text{(E-29)}$$

$$\bar{\chi}_{max} = \chi_{max}\ (0.35) \qquad \text{(E-30)}$$

Since the hazard factor is defined and derived from TLV values as follows:

$$F = (\text{TLV})\left(\frac{8}{24}\right)\left(\frac{1}{100}\right) \qquad \text{(E-31)}$$

$$F = (3.33 \times 10^{-3})\ \text{TLV} \qquad \text{(E-32)}$$

then the source severity, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.35)\chi_{max}}{(3.33 \times 10^{-3})\ TLV} \qquad (E\text{-}33)$$

$$S = \frac{105\ \chi_{max}}{TLV} \qquad (E\text{-}34)$$

If a weekly averaging period is used, then:

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3}{10080}\right)^{0.17} \qquad (E\text{-}35)$$

or

$$\bar{\chi}_{max} = (0.25)\chi_{max} \qquad (E\text{-}36)$$

and

$$F = (TLV)\left(\frac{40}{168}\right)\left(\frac{1}{100}\right) \qquad (E\text{-}37)$$

$$F = (2.38 \times 10^{-3})TLV \qquad (E\text{-}38)$$

and the source severity, S, is:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.25)\chi_{max}}{(2.38 \times 10^{-3})\ TLV} \qquad (E\text{-}39)$$

or

$$S = \frac{105\chi_{max}}{TLV} \qquad (E\text{-}40)$$

which is entirely consistent, since the TLV is being corrected for a different exposure period.

Therefore, the severity can be derived from χ_{max} directly without regard to averaging time for non-criteria emissions. Thus, combining Equations E-40 and E-26, for elevated source, gives:

$$S = \frac{5.5\ Q}{TLV \cdot H^2} \qquad \text{(H-41)}$$

b. Criteria Emissions

For the criteria pollutants, established standards may be used as F values in Equation E-27. These are given in Table H-4. However, Equation E-28 must be used to give the appropriate averaging period. These equations are developed for elevated sources using Equation E-26.

(1) CO Severity - The primary standard for CO is reported for a 1-hr averaging time. Therefore,

$$t = 60 \text{ min}$$
$$t_0 = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max}\left(\frac{3}{60}\right)^{0.17} \qquad \text{(E-42)}$$

$$= \frac{2\ Q}{\pi e u H^2}\left(\frac{3}{60}\right)^{0.17} \qquad \text{(E-43)}$$

$$= \frac{2\ Q}{(3.14)(2.72)(4.5)\ H^2}\ (0.6) \qquad \text{(E-44)}$$

$$= \frac{0.052\ Q}{H^2}\ (0.6) \qquad \text{(E-45)}$$

Table E-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS[38]

Pollutant	Averaging time	Primary standards	Secondary standards
Particulate matter	Annual (Geometric mean)	75 $\mu g/m^3$	60[a] $\mu g/m^3$
	24-hour[b]	260 $\mu g/m^3$	150 $\mu g/m^3$
Sulfur oxides	Annual (arithmetic mean)	80 $\mu g/m^3$ (0.03 ppm)	60 $\mu g/m^3$ (0.02 ppm)
	24-hour[b]	365 $\mu g/m^3$ (0.14 ppm)	260[c] $\mu g/m^3$ (0.1 ppm)
	3-hour[b]	-	1300 $\mu g/m^3$ (0.5 ppm)
Carbon monoxide	8-hour[b]	10 mg/m^3 (9 ppm)	
	1-hour[b]	40 mg/m^3 (35 ppm)	(Same as primary)
Nitrogen dioxide	Annual (arithmetic mean)	100 $\mu g/m^3$ (0.05 ppm)	(Same as primary)
Photochemical oxidants	1-hour[b]	160 $\mu g/m^3$ (0.08 ppm)	(Same as primary)
Hydrocarbons (nonmethane)	3-hour (6 to 9 a.m.)	160 $\mu g/m^3$ (0.24 ppm)	(Same as primary)

[a] The secondary annual standard (60 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the 24-hour secondary standard.

[b] Not to be exceeded more than once per year.

[c] The secondary annual standard (260 $\mu g/m^3$) is a guide for assessing implementation plans to achieve the annual standard.

- - - - - - - - - - -

[38] Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 p.

$$\bar{\chi}_{max} = \frac{(3.12 \times 10^{-2})Q}{H^2} \quad \text{(E-46)}$$

$$S = \frac{\bar{\chi}_{max}}{F} \quad \text{(E-47)}$$

Setting F equal to the primary standard for CO, i.e., 0.04 g/m^3 yields:

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(3.12 \times 10^{-2})Q}{0.04\ H^2} \quad \text{(E-48)}$$

or

$$S_{CO} = \frac{0.78\ Q}{H^2} \quad \text{(E-49)}$$

(2) Hydrocarbon Severity - The primary standard for hydrocarbon is reported for a 3-hr averaging time.

$$t = 180 \text{ min}$$

$$t_0 = 3 \text{ min}$$

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{180}\right)^{0.17} \quad \text{(E-50)}$$

$$= 0.5\chi_{max} \quad \text{(E-51)}$$

$$= \frac{(0.5)(0.052)\ Q}{H^2} \quad \text{(E-52)}$$

$$\bar{\chi}_{max} = \frac{0.026\ Q}{H^2} \quad \text{(E-53)}$$

For hydrocarbons, $F = 1.6 \times 10^{-4}$ g/m^3

and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.026\ Q}{1.6 \times 10^{-4} H^2} \qquad \text{(E-54)}$$

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \qquad \text{(E-55)}$$

(3) Particulate Severity - The primary standard for particulate is reported for a 24-hr averaging time.

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{3}{1440} \right)^{0.17} \qquad \text{(E-56)}$$

$$= \frac{(0.052)\ Q\ (0.35)}{H^2} \qquad \text{(E-57)}$$

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \qquad \text{(E-58)}$$

For particulates, $F = 2.6 \times 10^{-4}$ g/m^3

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \qquad \text{(E-59)}$$

$$S_P = \frac{70\ Q}{H^2} \qquad \text{(E-60)}$$

(4) SO_x Severity - The primary standard for SO_x is reported for a 24-hr averaging time.

$$\bar{\chi}_{max} = \frac{(0.0182)\ Q}{H^2} \qquad \text{(E-61)}$$

The primary standard is 3.65×10^{-4} g/m^3.

and

$$S = \frac{\bar{\chi}_{max}}{F} = \frac{(0.0182)\ Q}{3.65 \times 10^{-4}\ H^2} \qquad \text{(E-62)}$$

or

$$S_{SO_x} = \frac{50\ Q}{H^2} \qquad \text{(E-63)}$$

(5) NO_x Severity - Since NO_x has a primary standard with a 1-yr averaging time, the χ_{max} correction equation cannot be used. As an alternative, the following equation was selected:

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)\right]^2 \qquad \text{(E-64)}$$

A difficulty arises, however, because a distance x, from emission point to receptor, is included and hence, the following rationale is used:

The equation $\chi_{max} = \frac{2\ Q}{\pi e u H^2}$

is valid for neutral conditions or when $\sigma_z \approx \sigma_y$. This maximum occurs when

$$H \approx \sqrt{2}\sigma_z$$

and since, under these conditions,

$$\sigma_z = ax^b$$

then the distance x_{max} where the maximum concentration occurs is:

$$x_{max} = \left(\frac{H}{\sqrt{2}a} \right)^{\frac{1}{b}}$$

For class C conditions,

$$a = 0.113$$

$$b = 0.911$$

Simplifing Equation E-64

since $\sigma_z = 0.113\ x_{max}^{0.911}$

and $u = 4.5$ m/sec

Letting $x = x_{max}$ in Equation E-64,

$$\bar{\chi}_{max} = \frac{4\ Q}{x_{max}^{1.911}} \exp\left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right] \qquad \text{(E-65)}$$

$$x_{max} = \left(\frac{H}{0.16} \right)^{1.098} \qquad \text{(E-66)}$$

$$x_{max} = 7.5\ H^{1.098} \qquad \text{(E-67)}$$

and

$$\frac{4\ Q}{x_{max}^{1.911}} = \frac{4\ Q}{(7.5\ H^{1.098})^{1.911}} \qquad \text{(E-68)}$$

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(E-69)}$$

$$\sigma_z = 0.113x^{0.911} \qquad \text{(E-70)}$$

$$\sigma_z = 0.113\ (7.5\ H^{1.1})^{0.911} \qquad \text{(E-71)}$$

$$\sigma_z = 0.71\ H \qquad \text{(E-72)}$$

Therefore

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{0.71\ H}\right)^2\right] \qquad \text{(E-73)}$$

$$= \frac{0.085\ Q}{H^{2.1}}\ (0.371) \qquad \text{(E-74)}$$

and

$$\bar{\chi}_{max} = \frac{3.15 \times 10^{-2}\ Q}{H^{2.1}} \qquad \text{(E-75)}$$

Since the NO_x standard is 1.0×10^{-4} g/m^3, the NO_x severity equation is:

$$S_{NO_x} = \frac{(3.15 \times 10^{-2})\ Q}{1 \times 10^{-4}\ H^{2.1}} \qquad \text{(E-76)}$$

$$S_{NO_x} = \frac{315\ Q}{H^{2.1}} \qquad \text{(E-77)}$$

4. AFFECTED POPULATION CALCULATION

Another form of the plume dispersion equation is needed to calculate the affected population since the population is assumed to be distributed uniformly around the source. If the wind directions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration ($\bar{\chi}$) is then:[18]

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \quad (g/m^3) \qquad \text{(E-78)}$$

To find the distances at which $\bar{\chi}$/AAQS or $\bar{\chi}$/F = 1.0, roots are determined for the following equation:

$$0 = \left\{\frac{2.03\ Q}{AAQS\sigma_z ux} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right]\right\} - 1.0 \qquad \text{(E-79)}$$

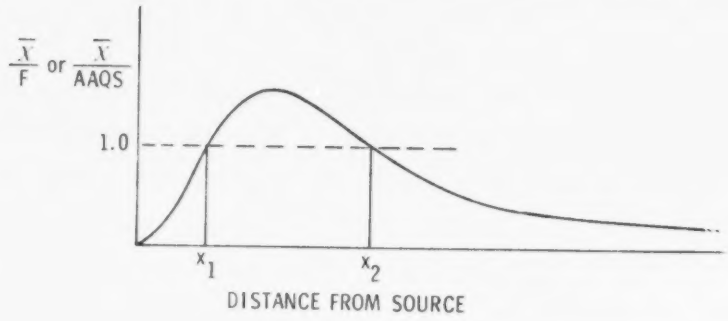
keeping in mind that:

$$\sigma_z = a\ x^{\,b} + c \qquad \text{(E-80)}$$

where a, b, and c are functions of atmospheric stability and are assumed to be for stability Class C.

Since equation E-79 is a transcendental equation the roots are found by an iterative technique using the computer.

For specified emission from a typical source, $\bar{\chi}$/AAQS or $\bar{\chi}$/F as a function of distance might look as follows:



The affected population is then in the area

$$A_p = \pi(x_2^2 - x_1^2) \qquad \text{(E-80)}$$

If the affected population density is D_p then the total affected population P is

$$P = D_p A_p \text{ (persons)} \qquad \text{(E-81)}$$

APPENDIX F

DERIVATION OF AVERAGE DISTANCE FROM A SOURCE TO A RECTANGULAR PLANT BOUNDARY

Consider a rectangular plant boundary of length "a" and width "b". An emission point is located within it with coordinates as shown in Figure F-1.

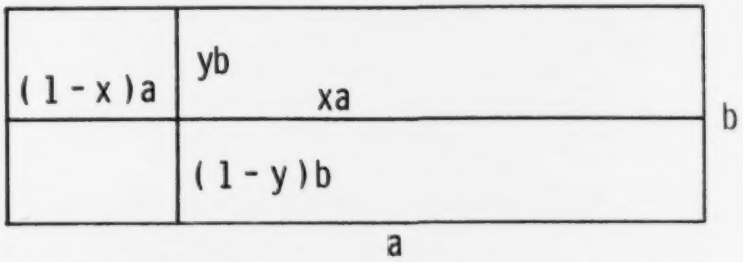


Figure F-1. Rectangular plant boundary

Here x, y, (1 - x), and (1 - y) are fractional distances to the sides.

$$0 \leq x,\ y,\ (1 - x),\ (1 - y) \leq 1$$

$$x + (1 - x) = 1$$

$$y = (1 - y) = 1$$

The average distance from the point to the boundary can be found from the integral

$$\int_0^{2\pi} R(\theta)d\theta \Big/ \int_0^{2\pi} d\theta$$

where R is the distance from the point to the perimeter of the rectangle.

The coordinate system with R and θ is shown in Figure F-2. Notice that R is a different function along each side of the rectangle. The line $\theta = 0$ is defined to be along the line segment xa.

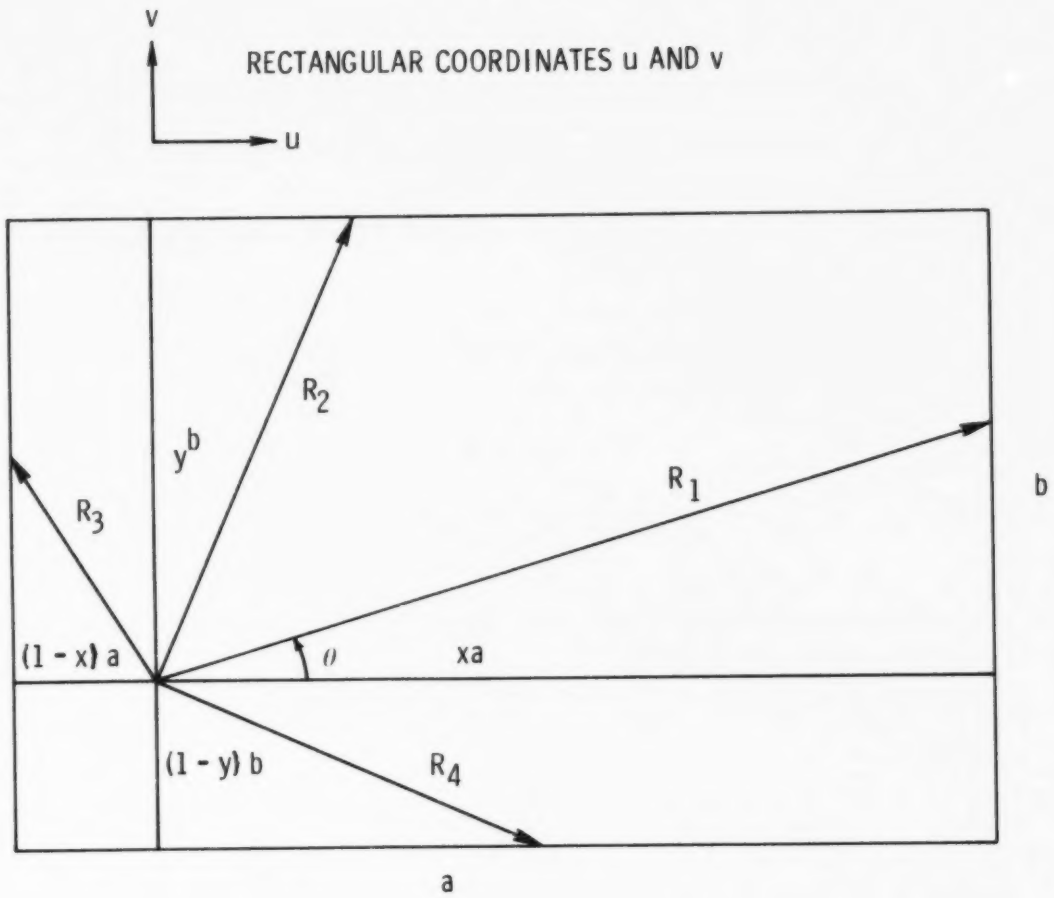


Figure F-2. Coordinate system for calculating average distance

The expression can then be written as:

$$\bar{D} = \frac{1}{2\pi} \int_0^2 (R_1 + R_2 + R_3 + R_4)\, d\theta \qquad \text{(F-1)}$$

This equation can be transformed into rectangular coordinates u, v by the substitution:

$$d\theta = \frac{udv - vdu}{u^2 + v^2} \qquad \text{(F-2)}$$

It becomes:

$$\bar{D} = \frac{1}{2\pi} \int_{-(1-y)b}^{yb} R_1 \frac{xa\, dv}{x^2a^2 + v^2} - \frac{1}{2\pi} \int_{xa}^{-(1-x)a} R_2 \frac{yb\, du}{y^2b^2 + u^2}$$

$$- \frac{1}{2\pi} \int_{yb}^{-(1-y)b} R_3 \frac{(1-x)a\, dv}{(1-x)^2a^2 + v^2}$$

$$+ \frac{1}{2\pi} \int_{-(1-x)a}^{xa} R_4 \frac{(1-y)b\, du}{(1-y)^2b^2 + u^2} \qquad \text{(F-3)}$$

The R functions can be defined from Figure F-2 in terms of u and v:

$$R_1 = \sqrt{x^2a^2 + v^2} \qquad \text{(F-4)}$$

$$R_2 = \sqrt{y^2b^2 + u^2} \qquad \text{(F-5)}$$

$$R_3 = \sqrt{(1-x)^2a^2 + v^2} \qquad \text{(F-6)}$$

$$R_4 = \sqrt{(1-y)^2b^2 + u^2} \qquad \text{(F-7)}$$

This yields:

$$\bar{D} = \frac{xa}{2\pi} \int_{-(1-y)b}^{yb} \frac{dv}{\sqrt{x^2a^2 + v^2}} - \frac{yb}{2\pi} \int_{xa}^{-(1-x)a} \frac{du}{\sqrt{y^2b^2 + u^2}}$$

$$- \frac{(1-x)a}{2\pi} \int_{yb}^{-(1-y)b} \frac{dv}{\sqrt{(1-x)^2a^2 + v^2}}$$

$$+ \frac{(1-y)b}{2\pi} \int_{-(1-x)a}^{xa} \frac{du}{\sqrt{(1-y)^2b^2 + u^2}} \qquad \text{(F-8)}$$

This integral can be evaluated by using:

$$\int \frac{du}{\sqrt{u^2 + k^2}} = \log_e \left(u + \sqrt{u^2 + k^2} \right) \qquad \text{(F-9}$$

which gives:

$$\bar{D} = \frac{xa}{2\pi} \log_e \left(v + \sqrt{v^2 + x^2a^2}\right)\Bigg|_{-(1-y)b}^{yb}$$

$$- \frac{yb}{2\pi} \log_e \left(u + \sqrt{u^2 + y^2b^2}\right)\Bigg|_{xa}^{-(1-x)b}$$

$$- \frac{(1-x)a}{2\pi} \log_e \left(v + \sqrt{v^2 + (1-x)^2a^2}\right)\Bigg|_{yb}^{-(1-y)b}$$

$$+ \frac{(1-y)b}{2\pi} \log_e \left(u + \sqrt{u^2 + (1-y)^2b^2}\right)\Bigg|_{-(1-x)a}^{xa} \qquad \text{(F-10)}$$

This simplifies to:

$$\bar{D} = \frac{xa}{2\pi} \log_e \frac{\sqrt{x^2a^2 + y^2b^2} + yb}{\sqrt{x^2a^2 + (1-y)^2b^2} - (1-y)b}$$

$$+ \frac{yb}{2\pi} \log_e \frac{\sqrt{x^2a^2 + y^2b^2} + xa}{\sqrt{(1-x)^2a^2 + y^2b^2} - (1-x)a}$$

$$+ \frac{(1-x)a}{2\pi} \log_e \frac{\sqrt{(1-x)^2a^2 + y^2b^2} + yb}{\sqrt{(1-x)^2a^2 + (1-y)^2b^2} - (1-y)b}$$

$$+ \frac{(1-y)b}{2\pi} \log_e \frac{\sqrt{x^2a^2 + (1-y)^2b^2} + xa}{\sqrt{(1-x)^2a^2 + (1-y)^2b^2} - (1-x)a} \qquad \text{(F-11)}$$

Example A: Square with edge of 2(= a = b)

Case I - Point at center (x = y = 1/2); xa = yb = 1

$$\bar{D} = \frac{4}{2\pi} \log_e \frac{\sqrt{2} + 1}{\sqrt{2} - 1} = 1.122$$

Case II - Point at corner (x = y = 0); xa = yb = 0
(1 - x)a = (1 - y)b = 2

$$\bar{D} = \frac{2}{\pi} \log_e \frac{\sqrt{4}}{\sqrt{8} - 2} = \frac{2}{\pi} \log_e \frac{1}{\sqrt{2} - 1} = 0.561$$

Example B: A rectangle with sides of 4(= a) and 1(= b)

Case I - Point in the center (x = y = 1/2);
xa = (1 - x)a = 2
yb = (1 - y)b = 1/2

$$\bar{D} = 0 + 0 + \frac{2}{\pi} \log_e \frac{\sqrt{4\ 1/4} + 1/2}{\sqrt{4\ 1/4} - 1/2} + \frac{2}{4\pi} \log_e \frac{\sqrt{4\ 1/4} + 2}{\sqrt{4\ 1/4} - 2}$$

$$\bar{D} = 0.3151 + 0.6668 = 0.982$$

Case II - Point at corner (x = y = 0); xa = yb = 0
(1 - x)a = 4
(1 - y)b = 1

$$\bar{D} = 0 + 0 + \frac{2}{\pi} \log_e \frac{\sqrt{16}}{\sqrt{17} - 1} + \frac{1}{2\pi} \log_e \frac{\sqrt{1}}{\sqrt{17} - 4}$$

$$\bar{D} = 0.1575 + 0.3334 = 0.491$$

Example C: Barium plant

$$xa = 1{,}750 \text{ ft}$$
$$(1 - x)a = 575 \text{ ft}$$
$$yb = 1{,}135 \text{ ft}$$
$$(1 - y)b = 175 \text{ ft}$$

$$\bar{D} = \frac{1{,}750}{2\pi} \log_e \frac{2{,}085.8 + 1{,}135}{1{,}758.7 - 175} + \frac{1{,}135}{2\pi} \log_e \frac{2{,}085.8 + 1{,}750}{1{,}272.3 - 575}$$

$$+ \frac{575}{2\pi} \log_e \frac{1{,}272.3 + 1{,}135}{601.0 - 175} + \frac{175}{2\pi} \log_e \frac{1{,}758.7 + 1{,}750}{601.0 - 577}$$

$$\bar{D} = 197.7 + 308.0 + 158.5 + 136.6 = 800.8 \text{ ft (244 m)}$$

APPENDIX G

PLUME RISE CORRECTION

The Gaussian plume equation that is used to predict ground level concentrations contains a factor called the effective stack height, H. This is equal to the physical stack height (h) plus the amount of plume rise (ΔH).

$$H = h + \Delta H$$

An exhaust plume rises before dispersal due to its exit velocity and temperature. In the case of barium chemicals this is not a significant effect ($\Delta H/h < 25\%$).

Plume rise can be estimated from the Holland formula[19]

$$\Delta H = \frac{V_s D_i}{u} \left(1.5 + 2.68 \times 10^{-3} p \frac{T_s - T_a}{T_s} D_i\right)$$

where V_s = stack gas exit velocity, m/sec
D_i = inside stack diameter, m
u = wind speed, m/sec
p = atmospheric pressure, mb
T_s = stack gas temperature, °K
T_a = ambient temperature, °K

Under C class stability conditions ΔH is increased by a correction factor of 1.10. The ambient temperature is taken to be 294°K (70°F), the wind speed 4.5 m/sec, and the pressure 1,013 mb.

For a black ash kiln, ΔH can be determined from the stack data in Table C-2. Here V_s = 13.2 m/s, d = 1.0 m, and

T_s = 455°K. The plume rise is then 7.9 m, compared to the actual stack height of 38.1 m. The ratio of ΔH/h is 21%.

Data for dryers and calciners appears in Table G-1.[11] For the rotary dryer and calciner, ΔH/h is only 2%. The drum dryer (the only one in the industry) has a larger plume rise (3.8 m), but the effective stack height (11.4 m) is close to the average stack height of 10 m used in calculating severity, S.

Table G-1. PLUME RISE FOR DRYERS AND CALCINERS[11]

Unit	Stack height, m	V_s, m/sec	d, m	T_s, °K	ΔH	ΔH/h
Rotary dryer	11.0	0.31	0.91	497	0.18	0.02
Rotary calciner	11.0	0.79	0.52	443	0.20	0.02
Drum dryer	7.6	24.31	0.40	330	3.8	0.50

SECTION VIII

GLOSSARY

BARITE - The ore from which barium chemicals are made; it is 90% to 95% $BaSO_4$.

BENEFICIATION - Processing of ore by physical means (e.g., grinding, washing) to remove impurities.

BLACK ASH - Barium sulfide produced by the reduction of barite with coal/coke; so called because of its black color.

CALCINING - Heating of barium carbonate to increase its bulk density; fine particles agglomerate to form larger ones.

CARCINOGEN - A chemical substance which causes cancer in animals or man.

FUGITIVE DUST - Dust emissions from a process that are not emitted from a stack or vent.

JIG - A mechanical device used for separating materials of different specific gravities by the pulsation of a stream of liquid through the bed of materials; employed in barite ore beneficiation.

LEACHING - Removal of a soluble component, in the form of a solution, from an insoluble solid phase with which it is associated.

LITHOPONE - A white pigment made of $BaSO_4$ and ZnS.

ORSAT ANALYSIS - A technique for measuring the composition of an exhaust gas by differential absorption of the components.

PETROLEUM COKE - The solid residue remaining from the refining of petroleum.

POLYNUCLEAR ORGANIC MATERIALS - Aromatic ring compounds containing three or more rings; some POM's [e.g., benzo(a)-pyrene] are known carcinogens.

ROTARY KILN - A high temperature process furnace lined with refractory material; it is an inclined cylinder that rotates on its axis.

SECTION IX

REFERENCES

1. Personal communications. J. L. Gray and R. E. Kotteman, Jr. Chemical Products Corp., Cartersville, Georgia.

2. Personal communications. R. Brown. FMC Corp., Modesto, California.

3. Personal communications. J. J. Nilles and R. W. Hellon. Sherwin-Williams Co., Coffeyville, Kansas.

4. Personal communications. D. Muller. Great Western Sugar Co., Johnstown, Colorado.

5. Fulkerson, F. B. Barite. In: Minerals Yearbook 1972, Volume I: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1974. p. 181-187.

6. Preisman, L. Barium Compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition. Vol. 3, Standen, A. (ed.). New York, Interscience Publishers, Division of John Wiley & Sons, Inc., 1964. p. 80-99.

7. Dahlberg, H. W., and R. J. Brown; revised by W. Newton, II, and M. G. Auth. The Barium Saccharate Process. In: Beet-Sugar Technology, Second Edition, McGinnis, R. A. (ed.). Fort Collins, Colorado, Beet Sugar Development Foundation, 1970. p. 573-578.

8. Particulate Polycyclic Organic Matter. Washington, National Academy of Sciences, 1972. 361 p.

9. Hangebrauch, R. P., D. J. Von Lehmden, and J. E. Meeker. Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat-Generation and Incinerator Processes. Journal of the Air Pollution Control Association. 14:267-278, July 1964.

10. The Toxic Substances List 1974 Edition, Christensen, H. E., and T. T. Luginbyhl (ed.). Rockville, Maryland, U.S. Department of Health, Education and Welfare, June 1974. 904 p.

11. Point Source Listing for Inorganic Pigments, SSC 3-01-035, National Emission Data System. Environmental Protection Agency. Research Triangle Park. August 1974.

12. TLV's® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists. Cincinnati. 1975. 97 p.

13. Pendergrass, E. P., and R. R. Greening. Baritosis. Archives of Industrial Hygiene and Occupational Medicine. 7:44-48, 1953.

14. Willson, J. K. V., P. S. Rubin, and T. M. McGee. The Effects of Barium Sulfate on the Lungs. American Journal of Roentgenology, Radium Therapy and Nuclear Medicine. 82:84-94, July 1959.

15. Gleason, M. N., R. E. Gosselin, and H. C. Hodge. Clinical Toxicology of Commercial Products. Baltimore, The Williams & Wilkins Co., 1957. p. 28-29, 120-121.

16. Barium and Its Inorganic Compounds. American Industrial Hygiene Association Journal. 23:517-518, November-December 1962.

17. Effect of Barium Carbonate Fumes on Respiratory Tract. Journal of the American Medical Association. 117:1221, 1941.

18. 1972 National Emissions Report. Environmental Protection Agency. Research Triangle Park. Publication No. EPA-450/2-74-012. June 1974. 422 p.

19. Turner, D. B. Workbook of Atmospheric Dispersion Estimates, 1970 Revision. U.S. Department of Health, Education, and Welfare. Cincinnati. Public Health Service Publication No. 999-AP-26. May 1970. 84 p.

20. Kaplan, N. An EPA Overview of Sodium-Based Double Alkali Processes - Part II - Status of Technology and Description of Attractive Schemes. In: Proceedings: Flue Gas Desulfurization Symposium-1973. Environmental Protection Agency. Research Triangle Park. Publication No. EPA-650/2-73-038. December 1973. p. 1019-1060.

21. Arundale, J. C., and F. M. Barsigian. Barite. In: Minerals Yearbook 1951. Washington, Bureau of Mines, 1954. p. 186-195.

22. Schreck, A. E., and J. M. Foley. Barite. In: Minerals Yearbook 1956, Volume I: Metals and Minerals. Washington, Bureau of Mines, 1958. p. 219-229.

23. Skow, M. L., and V. R. Schreck. Barite. In: Minerals Yearbook 1961, Volume I: Metals and Minerals. Washington, Bureau of Mines, 1962. p. 295-308.

24. Barite. In: Minerals Yearbook 1966, Volume I-II: Metals, Minerals, and Fuels. Washington, Bureau of Mines, 1967. p. 428-433.

25. Eilertsen, D. E. Barite. In: Minerals Yearbook 1967, Volume I-II: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1968. p. 209-215.

26. Diamond, W. G. Barite. In: Minerals Yearbook 1968, Volume I-II: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1969. p. 189-194.

27. Diamond, W. G. Barite. In: Minerals Yearbook 1969, Volume I-II: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1971. p. 193-198.

28. Fulkerson, F. B. Barite. In: Minerals Yearbook 1970, Volume I: Metals, Minerals, and Fuels. Washington, Bureau of Mines, 1972. p. 205-210.

29. Fulkerson, F. B. Barite. In: Minerals Yearbook 1971, Volume I: Metals, Minerals and Fuels. Washington, Bureau of Mines, 1973. p. 191-197.

30. Current Industrial Report, Inorganic Chemicals 1973. Washington, U.S. Bureau of the Census, 1975. 28 p.

31. Chemical Profile: Barium Carbonate. Chemical Marketing Reporter. 207(13):9, March 31, 1975.

32. Barium Chemical Producers See Future Demand Weakness. Chemical Marketing Reporter. 207(13):21, March 31, 1975.

33. Harness, C. L., and F. M. Barsigian. Barite. In: Minerals Yearbook 1946. Washington, Bureau of Mines, 1948. p. 161-173.

34. Federal Register. 36(247):24876-24895, December 23, 1971.

35. Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffustion Model for Estimating the Effects on Air Quality of One or More Sources. (Presented at 61st Annual Meeting of the Air Pollution Control Association, for NAPCA, St. Paul, 1968.) 18 p.

36. Tadmor, J. and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment. 3:688-689, 1969.

37. Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, Slade, D. A. (ed.). Oak Ridge, Tennessee, U.S. Atomic Energy Commission Technical Information Center. Publication No. TID-24190. July 1968. p. 113.

38. Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 p.